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(54) **Photothermographic or thermographic material**

(57) An image-recording material which has at least on one surface side of a support a thermosensitive recording element containing a scaly organic acid silver salt, a reducing agent for a silver ion, and a binder, or a photosensitive recording element containing a scaly or-

ganic acid silver salt, a reducing agent for a silver ion, photosensitive silver halide, and a binder, wherein the NH_4^+ content of all the layers on the surface side of the support which contains the thermosensitive recording element is from 0.08 to 3.4 mmol as the coating amount per m^2 of the support.

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Description

FIELD OF THE INVENTION

- 5 [0001] The present invention relates to an image-recording material, in particular, to a photothermographic or thermographic material excellent in silver tone.

BACKGROUND OF THE INVENTION

- 10 [0002] A photothermographic or thermographic material has been proposed for long and described, for example, in U.S. Patents 3,152,904 and 3,457,075, D. Klosterboer, Thermally Processed Silver System, "Imaging Processes and Materials", compiled by Sturge, V. Walworth, A. Shepp, 8th Ed., Neblette, p. 279 (1989). A photothermographic material generally has a photosensitive layer comprising a catalytically active amount of photocatalyst (e.g., silver halide), a reducing agent, a reducible silver salt (e.g., organic silver salt), and a toning agent which controls the tone of silver according to necessity dispersed in a binder matrix. A photothermographic material forms a silver image of black color by heating at high temperature (e.g., 80°C or more) after image exposure to cause an oxidation reduction reaction between silver halide or a reducible silver salt (functioning as an oxidizing agent) with a reducing agent. The oxidation reduction reaction is accelerated by the catalytic action of the latent image of the silver halide generated by exposure. Therefore, the silver image of black color is formed in the exposure region.
- 20 [0003] A photothermographic material is generally stored as a bulk product after coating until processed and shipped. The storage stability of a coated bulk product during that time is not good and the improvement of the storage stability is desired. Further, it is desired that the tint of a silver image is not varied by the photothermographic temperature.

SUMMARY OF THE INVENTION

- 25 [0004] An object of the present invention is to improve the storage stability of a coated bulk product and silver tone in a (photo)thermographic material, in particular, a photothermographic material.

[0005] The above object of the present invention has been achieved by the following means.

30 (1) An image-recording material which has at least on one surface side of a support a thermosensitive recording element containing a scaly organic acid silver salt, a reducing agent for a silver ion, and a binder, or a photosensitive recording element containing a scaly organic acid silver salt, a reducing agent for a silver ion, photosensitive silver halide, and a binder, wherein the NH_4^+ content of all the layers on the surface side of the support which has the thermosensitive or photosensitive recording element is from 0.06 to 3.4 mmol as the coating amount per m^2 of the support.

35 (2) The material as described in the above item (1), wherein the NH_4^+ content is from 0.55 to 2.9 mmol as the coating amount per m^2 of the support.

(3) The material as described in the above item (1) or (2), wherein the alkali metal ion content of all the layers on the surface side of the support which has the thermosensitive or photosensitive recording element is from 0.05 to 3.6 mmol as the coating amount per m^2 of the support.

40 (4) The material as described in the above item (3), wherein the alkali metal ion content is from 0.59 to 3.0 mmol as the coating amount per m^2 of the support.

(5) The material as described in any of the above item (3) or (4), wherein the alkali metal ion is Li^+ , Na^+ , or K^+ .

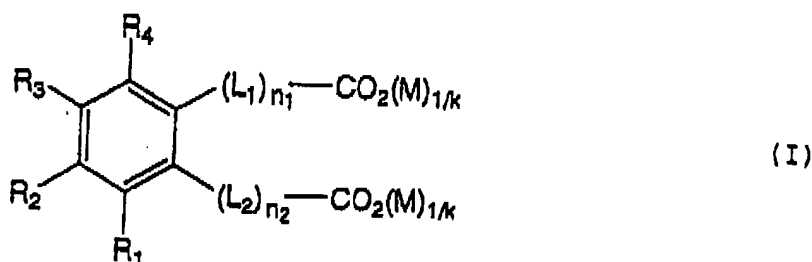
45 (6) The material as described in any of the above items (3) to (5), wherein the ratio of the contents of the alkali metal ion and NH_4^+ , i.e., $(\text{NH}_4^+)/(\text{alkali metal ion})$, is from 0.01 to 30 in molar ratio.

(7) The material as described in any of the above items (3) to (5), wherein the ratio of $(\text{NH}_4^+)/(\text{alkali metal ion})$ is from 0.1 to 20.

(8) The material as described in any of the above items (3) to (5), wherein the ratio of $(\text{NH}_4^+)/(\text{alkali metal ion})$ is from 0.5 to 5.

50 (9) The material as described in any of the above items (1) to (8), wherein the layer containing a scaly organic acid silver salt further contains a phthalic acid compound represented by formula (1):

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wherein R_1 , R_2 , R_3 and R_4 each represents a hydrogen atom or a monovalent substituent; L_1 and L_2 each represents a linking group; n_1 and n_2 each represents 0 or 1; M represents a hydrogen atom or a counter ion; and k represents a valency of M , and when M represents a hydrogen atom, k represents 1, provided that when M represents a hydrogen atom and n_1 and n_2 each represents 0, not all R_1 , R_2 , R_3 and R_4 represent a hydrogen atom.

(10) The material as described in the above item (9), wherein M in formula (I) represents an ammonium ion, an alkali metal ion, an alkaline earth metal ion, an aluminum ion, a zinc ion, an ionic polymer, an organic compound having reverse charge, or a metal complex ion.

(11) The material as described in any of the above items (1) to (10), wherein the silver behenate content of the organic acid silver salt is 92 mol% or more.

(12) The material as described in any of the above items (1) to (11), wherein the layer containing the scaly organic acid silver salt is formed by coating a coating solution in which 30% by weight or more of the solvent is occupied by water, and then drying, and the main binder of this layer is a polymer having an equilibrium moisture content at 25°C 60% RH of 2% by weight or less.

(13) The material as described in any of the above items (1) to (12), wherein the material contains a photosensitive recording element.

(14) The material as described in the above item (13), wherein the material has two or more constitutional layers including the photosensitive recording element on the same surface side of the support on which the photosensitive recording element is provided and these two or more constitutional layers are simultaneously coated.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Fig. 1 is a schematic cross-sectional view showing one example of a heat developing unit in a plate heater system for use in the present invention.

[0007] Fig. 2 is a schematic cross-sectional view showing another example of a heat developing unit in a plate heater system for use in the present invention.

Key to the Symbols

[0008]

18: Heat developing unit

120: Plate heater

122: Pressing roller

130: Driving roller

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present invention will be described in detail below.

[0010] The photothermographic material according to the present invention contains at least on one surface side of the support a scaly organic acid silver salt, a reducing agent for a silver ion, and a binder, and contains NH_4^+ in total of all the layers on the surface side of the support which contains the above components of from 0.06 to 3.4 mmol as the coating amount per m^2 of the support, or contains an alkali metal ion in total of all the layers on the surface side of the support which contains the above components of from 0.05 to 3.6 mmol as the coating amount per m^2 of the support. By using such a scaly organic acid silver salt and a prescribed amount of NH_4^+ or an alkali metal ion, less silver tone difference is generated due to heat development conditions, as a result good silver tone can be obtained by any heat development condition, thus a photothermographic material showing less photographic characteristic fluctuation due to the storage of a coated bulk product can be obtained. Contrary to this, when an acicular organic acid

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silver salt is used, not only the storage stability lowers but also the silver tone is deteriorated. On the other hand, if the amounts of NH_4^+ or an alkali metal ion are less than the above range, neither the silver tone is improved nor the storage stability is sufficient. While when the amounts of NH_4^+ or an alkali metal ion are larger than the above range, the storage stability decreases.

[0011] Further, it is also preferred to contain both NH_4^+ and an alkali metal ion for obtaining preferred silver tone and storage stability, and the ratio of $(\text{NH}_4^+)/(\text{alkali metal ion})$ is from 0.1 to 20.

[0012] Li^+ , Na^+ , or K^+ is preferred as the alkali metal ion for use in the present invention.

[0013] In the present invention, NH_4^+ and an alkali metal ion may be added as an alkali solution such as NH_4OH , alkali hydroxide metal ion (e.g., LiOH , NaOH , KOH) or they may be added in the form of a salt formed with an acid, alternatively they may be added as a salt formed with other photographically useful substances.

[0014] These compounds are added to the coating solution of the layer coated on the same surface side of the support as the layer containing an organic acid silver. When they are added as an alkali solution, a solution of from 0.1 to 40% by weight is preferably used, and when added in the form of a salt, any of a solution, a powder and a solid fine particle dispersion may be used.

[0015] The addition amount of NH_4^+ is from 0.06 to 3.4 mmol/m², preferably from 0.55 to 2.8 mmol/m², and the addition amount of an alkali metal ion is from 0.05 to 3.6 mmol/m², preferably from 0.59 to 3.0 mmol/m². They may be used NH_4^+ alone or an alkali metal ion alone but they are preferably used in combination, and the addition amount in this case is from 0.11 to 7.0 mmol/m², preferably from 1.14 to 6.4 mmol/m². The ratio of $(\text{NH}_4^+)/(\text{alkali metal ion})$ in this case is from 0.01 to 30, preferably from 0.1 to 20, and more preferably from 0.5 to 5.

[0016] NH_4^+ and an alkali metal ion may be added to any of an organic acid silver-containing layer, a photosensitive layer, an interlayer, or a protective layer, and they may be added to two or more layers.

[0017] It is also preferred that they are added to a photosensitive layer by being added to the main binder of a photosensitive layer, which will be described later, or added as a dicarboxylic acid salt used as a tone adjuster, which will be also described later.

[0018] The layer containing an organic acid silver salt (an image-recording layer) of the photothermographic material according to the present invention can be formed by water system coating with an environment-friendly coating solution in which 30% by weight or more of the solvent is occupied by water, and it is preferred to use a polymer having an equilibrium moisture content at 25°C 60% RH of 2% by weight or less, which is preferred for obtaining good photographic performances, as the main binder of this layer. The photothermographic material according to the present invention preferably has a photosensitive layer containing photosensitive silver halide provided on the same surface side of the support as the layer containing an organic acid silver salt. It is particularly preferred for the organic acid silver salt-containing layer to contain photosensitive silver halide. It is also preferred from the viewpoint of the production to use a hydrophilic binder as the main binder of the constituting layers such as interlayer and the protective layer which are provided on the same surface side as the organic acid silver salt-containing layer (preferably the photosensitive layer) and the organic acid silver salt-containing layer is coated simultaneously with these layers.

[0019] Photo-insensitive organic acid silver salts for use in the present invention are scaly and they are preferably contained in a photosensitive layer or a photo-insensitive layer. Organic acids for forming silver salts are preferably long chain fatty acids preferably having from 10 to 30 carbon atoms, and more preferably from 15 to 25 carbon atoms. Organic silver salt complexes may also be used. The ligands of complexes preferably have the total stability constant against silver ions of from 4.0 to 10.0. Organic silver salts are described in Research Disclosure, No. 17029 and ibid., No. 29983.

[0020] Examples of organic silver salts include silver salts of fatty acids (e.g., gallic acid, oxalic acid, behenic acid, stearic acid, palmitic acid, lauric acid), silver salts of carboxyalkylthioureas (e.g., 1-(3-carboxypropyl)thiourea, 1-(3-carboxypropyl)-3,3-dimethylthiourea), silver complexes of the polymerization reaction products of aldehydes (e.g., formaldehyde, acetaldehyde, butyraldehyde) with hydroxysubstituted aromatic carboxylic acids, silver salts of aromatic carboxylic acids (e.g., salicylic acid, benzoic acid, 3,5-dihydroxybenzoic acid, 5,5-thiodisalicylic acid), silver salts or silver complexes of thiones (e.g., 3-(2-carboxyethyl)-4-hydroxymethyl-4-thiazoline-2-thione, 3-carboxymethyl-4-thiazoline-2-thione), silver salts or silver complexes of nitrogen acids (e.g., imidazole, pyrazole, urazole, 1,2,4-thiazole, 1H-tetrazole, 3-amino-5-benzylthio-1,2,4-triazole, benzotriazole), silver salts of saccharin, silver salt of 5-chlorosalicylaldehyde, and silver salts of mercaptides.

[0021] In the present invention, scaly organic acid silver salts are selected from among these compounds. It is preferred to use scaly organic acid silver salts alone as organic silver salts, but the above organic silver salts may also be used in combination with organic acid silver salts if the amount is within the range of 30 wt% or less of the entire amount. Fatty acid silver is preferred as an organic acid silver salt, in particular, organic acid silver salts containing 92 mol% or more of silver behenate are preferred, and silver behenate is most preferred. Organic acid silver salts are preferably used in an amount of from 0.05 to 3 g/m², more preferably from 0.3 to 2 g/m², as a silver amount.

[0022] As scaly organic acid silver salts are used in the present invention, "scaly" is judged as follows: An organic acid silver salt is observed with an electron microscope, the shape of the organic acid silver salt particle is approximated

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to a rectangular parallelepiped, and when the sides of the rectangular parallelepiped are taken as a, b and c from the shortest (c may be equal to b), x is calculated from the shorter numeric values a and b as follows:

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$$x = b/a$$

x is obtained about 200 particles by the above equation, and when the average value is taken as x (average), those satisfy the relationship $x \text{ (average)} > 1.5$ are regarded as scaly particles, preferably $30 > x \text{ (average)} > 1.5$, more preferably $20 > x \text{ (average)} > 2.0$. In this connection, acicular is $1 < x \text{ (average)} < 1.5$.

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[0023] In a scaly particle, a can be regarded as a thickness of a tubular particle having a plane making b and c the sides as a main plane. The average of a is preferably from 0.01 to 0.23 μm , and more preferably from 0.1 to 0.20 μm . The average of c/b is preferably from 1 to 6, more preferably from 1.05 to 4, still more preferably from 1.1 to 3, and particularly preferably from 1.1 to 2.

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[0024] When an aqueous solution containing a water-soluble silver salt and an aqueous tertiary alcohol solution containing an organic acid alkali metal salt are reacted in a reaction vessel (including the step of adding the aqueous tertiary alcohol solution containing an organic acid alkali metal salt to the solution in the reaction vessel), scaly organic acid silver salt is preferably formed in a manner so as to make the temperature difference between the solution in the reaction vessel (preferably the aqueous solution containing a water-soluble silver salt added to the reaction vessel in advance, or in the case when the aqueous solution containing a water-soluble silver salt is not previously added but added simultaneously with the aqueous tertiary alcohol solution containing an organic acid alkali metal salt from the first, the solution in the reaction vessel is water or a mixed solvent of water and a tertiary alcohol as later described, further also in the case when the aqueous solution containing a water-soluble silver salt is added to the reaction vessel in advance, water or a mixed solvent of water and a tertiary alcohol may previously be added to the vessel) and the aqueous tertiary alcohol solution containing an organic acid alkali metal salt to be added to the reaction vessel from 20°C to 85°C. By maintaining the temperature difference during the addition of the aqueous tertiary alcohol solution containing an organic acid alkali metal salt, the crystal form of the organic acid silver salt is advantageously controlled.

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[0025] As this water-soluble silver salt, silver nitrate is preferred, and as the concentration of the water-soluble silver salt in the aqueous solution is preferably from 0.03 to 6.5 mol/liter, more preferably from 0.1 to 5 mol/liter, and the pH of the aqueous solution is preferably from 2 to 6, more preferably from 3.5 to 6.

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[0026] A tertiary alcohol having from 4 to 6 carbon atoms may be contained in the aqueous solution containing a water-soluble silver salt, and in such a case the content of the tertiary alcohol is 70% by volume or less, preferably 50% by volume or less, based on the total volume of the aqueous solution containing a water-soluble silver salt. The temperature of the solution is preferably from 0°C to 50°C, more preferably from 5°C to 30°C. When the aqueous solution containing a water-soluble silver salt is added simultaneously with the aqueous tertiary alcohol solution containing an organic acid alkali metal salt, the temperature is preferably from 5°C to 15°C as is described later.

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[0027] The alkali metal of the organic acid alkali metal salt is specifically Na or K. Organic acid alkali metal salt is produced by adding NaOH or KOH to an organic acid. It is preferred to make the weight of the alkali equivalent or less of the weight of the organic acid at that time to leave an unreacted organic acid. The residual organic acid amount at this time is from 3 to 50 mol%, preferably from 3 to 30 mol%, per mol of the entire organic acid. Further, alkali of the amount larger than the prescribed amount is added and the excess amount of alkali may be neutralized afterward by adding an acid such as a nitric acid or a sulfuric acid.

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[0028] Further, pH can be adjusted by the required characteristics of the organic acid silver salt. For pH adjustment, arbitrary acids and alkalis can be used.

[0029] There may be added to the aqueous solution containing a water-soluble silver salt, the aqueous tertiary alcohol solution containing an organic acid alkali metal salt, or the solution in the reaction vessel, for example, a compound represented by formula (1) as disclosed in JP-A-62-65035 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), an N heterocyclic compound having a water-soluble group as disclosed in JP-A-62-150240, an inorganic peroxide as disclosed in JP-A-50-101019, a sulfur compound as disclosed in JP-A-51-76319, a disulfide compound as disclosed in JP-A-57-643, or a hydrogen peroxide.

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[0030] The aqueous tertiary alcohol solution containing an organic acid alkali metal salt according to the present invention is preferably a mixed solvent of a tertiary alcohol having from 4 to 6 carbon atoms and water for obtaining the homogeneity of the solution. If the carbon atom number exceeds this range, the compatibility with water is deteriorated, which is not advantageous. Of tertiary alcohols having from 4 to 6 carbon atoms, tert-butanol which is most compatible with water is most preferred. Since alcohols other than tertiary alcohols have reducibility, harmful influences are disadvantageously caused in the organic acid metal salt formation as described above. The content of the tertiary alcohols contained in the aqueous tertiary alcohol solution containing an organic acid alkali metal salt is from 3 to 70%, preferably from 5 to 50%, by volume of the solvent based on the volume of the water content in the aqueous tertiary alcohol solution.

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[0031] The concentration of the organic acid alkali metal salt in the aqueous tertiary alcohol solution containing an organic acid alkali metal salt for use in the present invention is from 7 to 50 wt%, preferably from 7 to 45 wt%, and more preferably from 10 to 40 wt%, by weight ratio.

[0032] The temperature of the aqueous tertiary alcohol solution containing an organic acid alkali metal salt added to the reaction vessel is preferably from 50 to 90°C, more preferably from 60 to 85°C, and most preferably from 65 to 85°C, for the purpose of maintaining the necessary temperature to prevent phenomena such as crystallization and solidification of the organic acid alkali metal salt. The temperature is preferably controlled at a certain temperature selected from the above range throughout the reaction.

[0033] The organic acid silver salt according to the present invention is produced by i) the method in which the total amount of the aqueous solution containing a water-soluble silver salt is added to the reaction vessel in advance and then the aqueous tertiary alcohol solution containing an organic acid alkali metal salt is added thereto (a single addition method), or ii) the method in which the aqueous solution containing a water-soluble silver salt and the aqueous tertiary alcohol solution containing an organic acid alkali metal salt are added simultaneously at least for some period of time (a simultaneous addition method). The latter simultaneous addition method is preferably used in the present invention for controlling the average particle size of the organic acid silver salt and making the particle size distribution narrow. In such a case, preferably 30 vol% or more, more preferably from 50 to 75 vol%, of the total addition amount is added simultaneously. When either one is added beforehand, the aqueous solution containing a water-soluble silver salt is preferably added first.

[0034] In any case, the temperature of the solution in the reaction vessel (the aqueous solution containing a water-soluble silver salt added in advance, or when the aqueous solution containing a water-soluble silver salt is not added precariously, the solvent previously added in the reaction vessel) is preferably from 5°C to 75°C, more preferably from 5°C to 60°C, and most preferably from 10°C to 50°C. The temperature is preferably controlled at a certain temperature selected from the above range throughout the reaction, but it is also preferred to control the temperature in some patterns within the above range.

[0035] In the present invention, the temperature difference between the aqueous tertiary alcohol solution containing an organic acid alkali metal salt and the solution in the reaction vessel is preferably from 20°C to 85°C, more preferably from 30°C to 80°C. In this case, it is preferred that the temperature of the aqueous tertiary alcohol solution containing an organic acid alkali metal salt is higher than that of the solution in the reaction vessel.

[0036] Thus, the rate of crystallite-like precipitation of the aqueous tertiary alcohol solution containing an organic acid alkali metal salt of high temperature as a result of sudden quenching in the reaction vessel and the rate of coming into an organic acid silver salt by the reaction with the water-soluble silver salt are preferably controlled. As a result, the crystal shape and the crystal size of the organic acid silver salt and the crystal size distribution can be preferably controlled. At the same time, the characteristics of the photothermographic material, in particular, the photothermographic photosensitive material, can be further improved.

[0037] A solvent may be put in a reaction vessel in advance, e.g., water is preferably used as a solvent previously added and a mixed solvent of a tertiary alcohol with water is also preferably used.

[0038] A dispersing aid which is soluble in an aqueous medium can be added to the aqueous tertiary alcohol solution containing an organic acid alkali metal and the aqueous solution containing a water-soluble silver salt according to the present invention, or the reaction solution. Any compound can be used as the dispersing aid so long as it can disperse the organic acid silver salt formed. Specific examples correspond to the dispersing aids of organic acid silver salts described later.

[0039] In the preparing method of the organic acid silver salt according to the present invention, it is preferred to perform desalting/dehydrating process after silver salt formation. Methods of desalting/dehydrating are not particularly restricted and well-known conventional means can be utilized. For example, well-known filtration methods such as centrifugal filtration, suction filtration, ultrafiltration, and washing of floc formed by agglomeration can be preferably used. The removal of a supernatant by centrifugal separation precipitation is also preferably used. Desalting/dehydrating may be performed only one time or may be repeated a plurality of times. Addition and removal of water may be performed continuously or separately. Desalting/dehydrating is performed until the conductivity of the dehydrated water finally reaches preferably 300 $\mu\text{S}/\text{cm}$ or less, more preferably 100 $\mu\text{S}/\text{cm}$ or less, and most preferably 60 $\mu\text{S}/\text{cm}$ or less. The lower limit of the conductivity in this case is not particularly limited but is generally about 5 $\mu\text{S}/\text{cm}$.

[0040] Further, for improving the coating surface condition of a photothermographic material, in particular, a photothermographic photosensitive material, it is preferred to prepare a water dispersion of an organic acid silver salt, convert the obtained dispersion to high pressure and high flow rate, and redisperse by pressure drop to obtain a fine water dispersion. The dispersion medium at this time is preferably water alone, but an organic solvent may be contained if the amount is 20 wt% or less.

[0041] An organic acid silver salt can be mechanically finely dispersed in the presence of a dispersing aid using well-known dispersing means (e.g., a high speed mixer, a homogenizer, a high speed impacting mill, a banbury mixer, a homomixer, a kneader, a ball mill, a vibrating ball mill, a planetary ball mill, an attritor, a sand mill, a beads mill, a colloid

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mill, a jet mill, a roller mill, a trommel and a high speed stone mill).

[0042] For obtaining fine particles of an organic acid silver salt having a small particle size and without agglomeration which can be used in the present invention, a method of obtaining a solid fine particle dispersion with a dispersant is used in the present invention. After the water dispersion of an organic acid silver salt obtained by the method of the present invention is converted to high pressure/high flow rate, a method of redispersing the dispersion by pressure drop is preferably used.

[0043] Further, if a photosensitive silver salt is present with the organic acid silver salt during dispersion, fog increases and sensitivity extremely lowers. Thus, it is more preferred not to substantially contain a photosensitive silver salt in the water dispersion solution. The content of a photosensitive silver salt in the water dispersion solution to be dispersed is 0.1 mol% or less per mol of the organic acid silver salt in the solution, where the addition of a photosensitive silver salt is not performed positively.

[0044] Solid dispersing apparatuses and techniques for performing the foregoing dispersion are described in detail, for example, in Toshio Kajuchi, Hiroshi Usui, Rheology of Dispersion System and Techniques of Dispersion, pp. 357 to 403, Shinoyama Publishing Co., Ltd. (1991), Advancement of Chemical Engineering, the 24th Series, pp. 184 and 185, compiled by the Tokai Branch of the Chemical Engineering Society, published by Maki Shoten (1990), JP-A-59-49832, U.S. Patent 4,533,254, JP-A-8-137044, JP-A-8-238848, JP-A-2-281525, JP-A-1-84933, etc. The redispersing method according to the present invention is a method in which a water dispersion solution containing at least an organic acid silver salt is fed to piping by high pressure using a high pressure pump and the like, passed through a fine slit in the piping, and then the pressure applied to the dispersion solution is suddenly reduced to thereby effect fine dispersion.

[0045] The reason why the dispersion to fine particles can be brought about by using a high pressure homogenizer is thought to be due to dispersion forces such as (a) "shear force" generated when a dispersoid passes through a narrow gap at high pressure and a high flow rate, and (b) "cavitation force" generated when the dispersoid is released from high pressure to atmospheric pressure. As a dispersing apparatus of this type, a Gaulin homogenizer has so far been used, wherein a dispersoid fed at high pressure is converted to high flow rate in a narrow gap on cylindrical plane, the dispersoid is impinged against the surrounding walls by that force, and emulsification and dispersion are effected by that impact force. The applied pressure is in general within the range of from 100 to 800 kg/cm² and a flow rate is from several meters to 30 meters/second, and some means have been elaborated to heighten a dispersion efficiency, such as to provide sawtooth blades at high flow rate zone to increase the number of times of impinging. On the other hand, apparatuses which make it possible to realize dispersion at higher pressure and a higher flow rate have been developed. By way of representative examples, a micro-fluidizer (manufactured by Micro Fluidex International Corp.) and a nanomizer (manufactured by Tokushu Kika Kogyo Co., Ltd.) are exemplified.

[0046] In the present invention, it is possible to achieve the dispersion of the organic acid silver salt of the desired particle size by adjusting flow rate, differential pressure at the time of pressure drop, and the number of times of processing. From the viewpoint of the photographic characteristics and the particle size, the flow rate is preferably from 200 to 800 m/second, more preferably from 300 to 600 m/second, and differential pressure at pressure drop is preferably from 900 to 3,000 kg/cm², more preferably from 1,500 to 3,000 kg/cm². The number of times of dispersion processing can be selected according to necessity and, in general, from 1 to 10 times, but in view of productivity, preferably from 1 to 3 or so. It is not preferred in the light of dispersion properties and photographic characteristics to maintain the temperature of a water dispersion solution high under high pressure, and when the temperature exceeds 90°C, the particle size is liable to increase and fog is also liable to increase. Accordingly, it is preferred in the present invention to include a cooling process in steps prior to conversion to high pressure/high flow rate, after pressure drop, or in both steps, to thereby maintain the temperature of the water dispersion preferably from 5 to 90°C, more preferably from 5 to 80°C, and particularly preferably from 5 to 85°C. In particular, it is effective to provide such a cooling process during high pressure dispersion of from 1,500 to 3,000 kg/cm². A cooler can be arbitrarily selected from, e.g., a double pipe and a triple pipe using a static mixer, a multitubular heat exchanger, and a coiled heat exchanger, according to the required heat exchange amount. Further, for increasing heat exchange efficiency, it is necessary to select appropriate diameter, thickness and material of the pipe with taking the pressure used into consideration. As a cooling medium in a cooler, well water of 20°C, chilled water of from 5 to 10°C treated with a refrigerator, or, if necessary, a cooling medium such as ethylene glycol/water of -30°C can be used according to heat exchange amount.

[0047] When a solid fine particle atomization of an organic acid silver salt is carried out using a dispersant, the following dispersants can be arbitrarily selected, e.g., synthetic anion polymers such as polyacrylic acid, acrylic acid copolymers, maleic acid copolymers, maleic acid monoester copolymers, and acryloylmethylpropane sulfonic acid copolymers, semi-synthetic anion polymers such as carboxymethyl starch and carboxymethyl cellulose, anionic polymers such as alginate acid and pectic acid, anionic surfactants disclosed in JP-A-52-92716 and WO 88/04794, compounds disclosed in JP-A-7-350753, well-known anionic, nonionic and cationic surfactants, other well-known polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, carboxymethyl cellulose, hydroxypropyl cellulose, and hydroxypropylmethyl cellulose, and natural high molecular compounds such as gelatin.

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[0048] A dispersing aid is in general mixed with the powder of an organic acid silver salt or an organic acid silver salt in a wet cake-like state before dispersion and fed to a dispersing apparatus as a slurry. Alternatively, a dispersing aid may be previously mixed with an organic acid silver salt and subjected to heat treatment or treatment with a solvent and then made into an organic acid silver salt powder or wet cake. pH adjustment may be performed before, after or during dispersion with an appropriate pH adjustor.

[0049] In addition to mechanical dispersion, organic acid silver salt may be coarsely dispersed in a solvent by pH controlling, and then atomized by changing pH in the presence of a dispersing aid. At this time, an organic solvent may be used for coarse dispersion and the organic solvent is in general removed after completion of the atomization.

[0050] The prepared dispersion can be preserved with stirring or in a highly viscous state with hydrophilic colloid (for example, in a jelly-like state using gelatin) for the purpose of preventing the precipitation of fine particles during preservation. Further, it is preferred to add preservatives for inhibiting the proliferation of various bacteria.

[0051] The organic acid silver salt prepared according to the producing method of the organic acid silver salt of the present invention is preferably dispersed in a water solvent, mixed with an aqueous photosensitive silver salt solution, and supplied as a coating solution for a photosensitive image-forming medium.

[0052] Examples of reducing agents preferably used in the present invention include phenidone, hydroquinones, catechol and hindered phenol. With respect to reducing agents, U.S. Patents 3,770,448, 3,773,512, 3,593,863, 4,460,681, and Research Disclosure, No. 17029 and ibid., No. 29963 can be referred to.

[0053] Specific examples of reducing agents include an aminohydroxycycloalkanone compound (e.g., 2-hydroxypiperidino-2-cyclohexenone), an N-hydroxyurea derivative (e.g., N-p-methylphenyl-N-hydroxyurea), hydrazones of aldehyde or ketone (e.g., anthracenealdehydephenylhydrazones), phosphor amidophenols, phosphor amidoanilines, polyhydroxybenzenes (e.g., hydroquinone, t-butylhydroquinone, isopropylhydroquinone, 2,5-dihydroxyphenylmethylsulfone), sulfohydroxamic acids (e.g., benzenesulfohydroxamic acid), sulfonamidoanilines (e.g., 4-(N-methanesulfonamido)aniline), 2-tetrazolythiohydroquinones (e.g., 2-methyl-5-(1-phenyl-5-tetrazolythio)hydroquinone), tetrahydroquinoxalines (e.g., 1,2,3,4-tetrahydroquinoxaline), amldoxines, combinations of azines (e.g., aliphatic carboxylic acid arylhydrazides) with ascorbic acid, combinations of polyhydroxybenzene hydroxylamines, reductone, hydrazine, hydroxamic acids, combinations of azines with sulfonamidophenols, an α -cyanophenylacetic acid derivative, combinations of bis- β -naphthol with a 1,3-dihydroxybenzene derivative, 5-pyrazolones, sulfonamidophenols, 2-phenylindane-1,3-dione, chroman, 1,4-dihydropyridines (e.g., 2,6-dimethoxy-3,5-dicarboethoxy-1,4-dihydropyridine), bisphenols (e.g., bis(2-hydroxy-3-t-butyl-5-methylphenyl)methane, bis(6-hydroxy-m-tri)mesitol, 2,4-bis(4-hydroxy-3-methylphenyl)propane, 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane, 4,4-ethylidene-bis(2-t-butyl-6-methylphenol), UV-sensitive ascorbic acid derivatives, and 3-pyrazolidones.

[0054] Esters of amino reductones which function as a reducing agent precursor (e.g., piperidinohexose reductone monoacetate) may be used as a reducing agent.

[0055] A particularly preferred reducing agent is hindered phenol.

[0056] The addition amount of a reducing agent is preferably from 0.01 to 5.0 g/m², more preferably from 0.1 to 3.0 g/m².

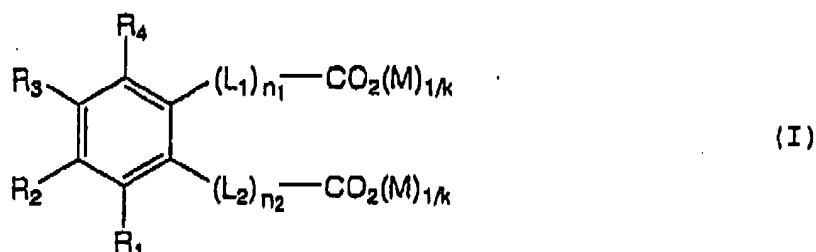
[0057] The photothermographic material according to the present invention comprises a support having provided thereon a layer containing a scaly organic acid silver salt (i.e., an image-recording layer); and contains a reducing agent for a silver ion and a binder, and preferably a phthalic acid compound represented by formula (I) on the same surface side of the support as the layer containing an organic acid silver salt. The photothermographic material according to the present invention is preferably a photothermographic photosensitive material which contains a photosensitive silver halide on the same surface side of the support as the layer containing an organic acid silver salt. Particularly preferably the organic acid silver salt-containing layer contains a photosensitive silver halide. Still more preferably a reducing agent for a silver ion is also contained in the same layer. In this photothermographic photosensitive material, by using a scaly organic acid silver salt as an organic acid silver salt and a phthalic acid compound represented by formula (I), less silver tone difference is generated due to heat development conditions, as a result good silver tone can be obtained by any heat development condition, thus a photothermographic material showing less photographic characteristic fluctuation due to the storage can be obtained. Contrary to this, when an acicular organic acid silver salt is used, not only the storage stability lowers but also the silver tone is deteriorated. On the other hand, when a compound such as a phthalic acid which is different from the phthalic acid compound represented by formula (I) alone is used, the silver tone is in particular deteriorated.

[0058] For improving the storage stability, organic acid silver salts containing 92 mol% or more of a silver behenate are preferably used. Further, the organic acid silver salt-containing layer can be formed by water system coating with an environment-friendly coating solution in which 30% by weight or more of the solvent is occupied by water, and it is preferred to use a polymer having an equilibrium moisture content at 25°C 60% RH of 2% by weight or less, which is preferred for obtaining good photographic performances, as the main binder of this layer. It is also preferred from the viewpoint of the production to use a hydrophilic binder as the main binder of the interlayer and the protective layer which are provided on the same surface side as the organic acid silver salt-containing layer and the organic acid silver

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salt-containing layer is coated simultaneously with these constituting layers.

[0059] A phthalic acid compound represented by formula (I) will be described in detail below.



wherein R_1 , R_2 , R_3 and R_4 each represents a hydrogen atom or a monovalent substituent; n_1 and n_2 each represents 0 or 1; M represents a hydrogen atom or a counter ion, provided that when M represents a hydrogen atom and n_1 and n_2 each represents 0, not all R_1 , R_2 , R_3 and R_4 represent a hydrogen atom. Examples of monovalent substituents represented by R_1 , R_2 , R_3 and R_4 include an alkyl group (preferably an alkyl group having from 1 to 20, more preferably from 1 to 12, and particularly preferably from 1 to 8, carbon atoms, e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-octyl, n-decyl, n-hexadecyl, cyclopropyl, cyclopentyl, cyclohexyl), an alkenyl group (preferably an alkenyl group having from 2 to 20, more preferably from 2 to 12, and particularly preferably from 2 to 8, carbon atoms, e.g., vinyl, allyl, 2-butenyl, 3-pentenyl), an alkynyl group (preferably an alkynyl group having from 2 to 20, more preferably from 2 to 12, and particularly preferably from 2 to 8, carbon atoms, e.g., propargyl, 3-pentynyl), an aryl group (preferably an aryl group having from 6 to 30, more preferably from 6 to 20, and particularly preferably from 6 to 12, carbon atoms, e.g., phenyl, p-methylphenyl, naphthyl), an amino group (preferably an amino group having from 0 to 20, more preferably from 0 to 10, and particularly preferably from 0 to 6, carbon atoms, e.g., amino, methylamino, dimethylamino, diethylamino, dibenzylamino), an alkoxy group (preferably an alkoxy group having from 1 to 20, more preferably from 1 to 12, and particularly preferably from 1 to 8, carbon atoms, e.g., methoxy, ethoxy, butoxy, benzyloxy), an aryloxy group (preferably an aryloxy group having from 6 to 20, more preferably from 6 to 16, and particularly preferably from 6 to 12, carbon atoms, e.g., phenyloxy, 2-naphthyloxy), an acyl group (preferably an acyl group having from 1 to 20, more preferably from 1 to 16, and particularly preferably from 1 to 12, carbon atoms, e.g., acetyl, benzoyl, formyl, pivaloyl), an alkoxycarbonyl group (preferably an alkoxycarbonyl group having from 2 to 20, more preferably from 2 to 16, and particularly preferably from 2 to 12, carbon atoms, e.g., methoxycarbonyl, ethoxycarbonyl, tetrade-cyloxy carbonyl), an aryloxy carbonyl group (preferably an aryloxy carbonyl group having from 7 to 20, more preferably from 7 to 16, and particularly preferably from 7 to 10, carbon atoms, e.g., phenyloxy carbonyl), an acyloxy group (preferably an acyloxy group having from 2 to 20, more preferably from 2 to 16, and particularly preferably from 2 to 10, carbon atoms, e.g., acetoxyl, benzoyloxy), an acylamino group (preferably an acylamino group having from 2 to 20, more preferably from 2 to 16, and particularly preferably from 2 to 10, carbon atoms, e.g., acetylamino, propionylamino, benzoylamino), an alkoxycarbonylamino group (preferably an alkoxycarbonylamino group having from 2 to 20, more preferably from 2 to 16, and particularly preferably from 2 to 12, carbon atoms, e.g., methoxycarbonylamino), an aryloxy carbonylamino group (preferably an aryloxy carbonylamino group having from 7 to 20, more preferably from 7 to 16, and particularly preferably from 7 to 12, carbon atoms, e.g., phenyloxy carbonylamino), a sulfonylamino group (preferably a sulfonylamino group having from 1 to 20, more preferably from 1 to 16, and particularly preferably from 1 to 12, carbon atoms, e.g., methanesulfonylamino, octanesulfonylamino, benzenesulfonylamino), a sulfamoyl group (preferably a sulfamoyl group having from 0 to 20, more preferably from 0 to 16, and particularly preferably from 0 to 12, carbon atoms, e.g., sulfamoyl, methylsulfamoyl, dimethylsulfamoyl, phenylsulfamoyl), a carbamoyl group (preferably a carbamoyl group having from 1 to 20, more preferably from 1 to 16, and particularly preferably from 1 to 12, carbon atoms, e.g., carbamoyl, methylcarbamoyl, diethylcarbamoyl, phenylcarbamoyl), an alkylthio group (preferably an alkylthio group having from 1 to 20, more preferably from 1 to 16, and particularly preferably from 1 to 12, carbon atoms, e.g., methylthio, ethylthio), an arylthio group (preferably an arylthio group having from 6 to 20, more preferably from 6 to 16, and particularly preferably from 6 to 12, carbon atoms, e.g., phenylthio), a sulfonyl group (preferably a sulfonyl group having from 1 to 20, more preferably from 1 to 16, and particularly preferably from 1 to 12, carbon atoms, e.g., mesyl, tosyl), a sulfinyl group (preferably a sulfinyl group having from 1 to 20, more preferably from 1 to 16, and particularly preferably from 1 to 12, carbon atoms, e.g., methanesulfinyl, benzenesulfinyl), a ureido group (preferably a ureido group having from 1 to 20, more preferably from 1 to 16, and particularly preferably from 1 to 12, carbon atoms, e.g., ureido, methylureido, phenylureido), a phosphoric acid amide group (preferably a phosphoric acid amide

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group having from 1 to 20, more preferably from 1 to 16, and particularly preferably from 1 to 12, carbon atoms, e.g., diethylphosphoric acid amide, phenylphosphoric acid amide), a hydroxyl group, a carboxyl group, a sulfo group, a sulfinio group (a sulfinic acid group), a mercapto group, a halogen atom (e.g., fluorine, chlorine, bromine, iodine), a cyano group, a nitro group, a hydroxamic acid group, a hydrazino group, and a heterocyclic group (e.g., imidazolyl, pyridyl, furyl, piperidyl, morpholino). A substituent which can form a salt with, e.g., an alkali metal, may form a salt. These substituents may further be substituted. When there are two or more substituents, they may be the same or different.

[0060] Preferred examples of the substituents represented by R_1 , R_2 , R_3 and R_4 include an alkyl group, an alkenyl group, an aryl group, an alkoxy group, an aryloxy group, an acyl group, an acyloxy group, an alkoxy carbonyl group, an acylamino group, an alkoxy carbonylamino group, an aryloxy carbonylamino group, a sulfonylamino group, a sulfamoyl group, a carbamoyl group, a ureido group, a phosphoric acid amide group, a hydroxyl group, a carboxyl group, a sulfo group, a sulfinio group, a sulfonyl group, a halogen atom, a cyano group, a nitro group, and a heterocyclic group. More preferred groups include an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an acyl group, an acylamino group, a sulfonylamino group, a sulfamoyl group, a carbamoyl group, a hydroxyl group, a sulfonyl group, a halogen atom, and a cyano group, and particularly preferred groups include an alkyl group, an aryl group, an alkoxy group, and a halogen atom.

[0061] R_1 , R_2 , R_3 and R_4 each particularly preferably represents a hydrogen atom or the above-exemplified particularly preferred substituent.

[0062] L_1 and L_2 each represents a linking group. Linking groups represented by L_1 and L_2 are preferably divalent linking groups having from 1 to 6 carbon atoms. Preferred examples include an alkylene group having from 1 to 6 carbon atoms (e.g., $-CH_2-$, $-CH_2CH_2-$), $-C=O-$, $-CONH-$, $-SO_2NH-$, $-COO-$, $-O-$, and combinations of them. More preferred are alkylene groups having from 1 to 3 carbon atoms, and they may further have a substituent.

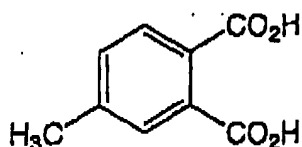
[0063] n_1 and n_2 each represents 0 or 1, preferably n_1 and n_2 each represents 0. When n_1 and n_2 each represents 1, L_1 and L_2 may be the same or different.

[0064] M represents a hydrogen atom or a counter ion, and k represents a valency of M , and when M represents a hydrogen atom, k represents 1. Examples of counter ions include an inorganic or organic ammonium ion (e.g., an ammonium ion, a triethylammonium ion, a pyridinium ion), an alkali metal ion (e.g., a lithium ion, a sodium ion, a potassium ion), an alkaline earth metal ion (e.g., a calcium ion, a barium ion, a magnesium ion), and other ions (e.g., an aluminum ion, a zinc ion). As counter ions, ionic polymers, other organic compounds having reverse charge, or a metal complex ion (e.g., a hydroxopentaaqua aluminum(III) ion, a tris(2,2'-bipyridine) iron(II) ion) are also applicable. M may form an inner salt with other substituent in the molecule. Preferred examples include a sodium ion, a potassium ion, an ammonium ion, a triethylammonium ion, and a pyridinium ion, and more preferred are a sodium ion, a potassium ion and an ammonium ion. In the present invention, M preferably represents a counter ion. When there are two M 's, they are in general the same but may be different in certain cases.

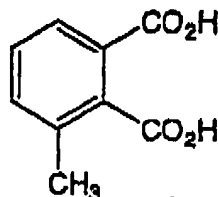
[0065] Specific examples of the compounds represented by formula (I) are shown below, but the present invention is not limited thereto.

Ammonium phthalate, sodium phthalate, potassium phthalate, lithium phthalate,

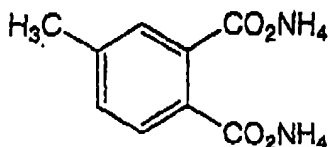
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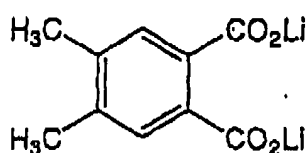
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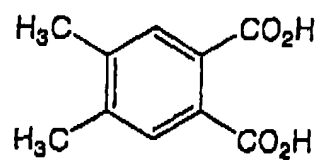


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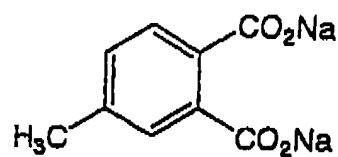


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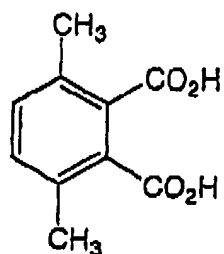
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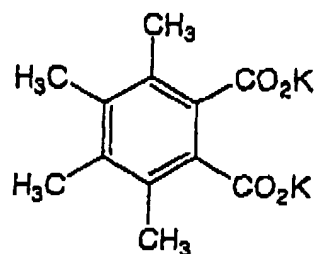
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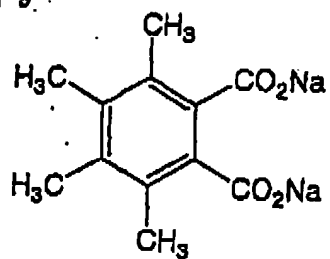
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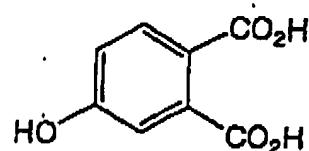
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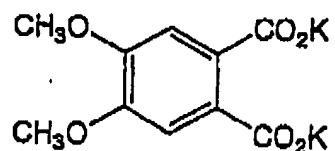
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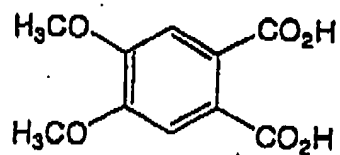
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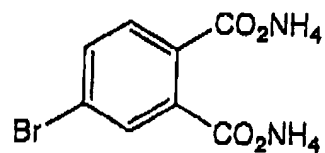
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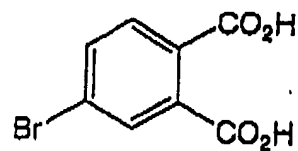
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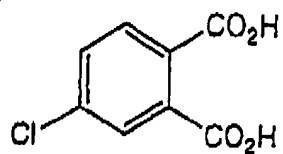


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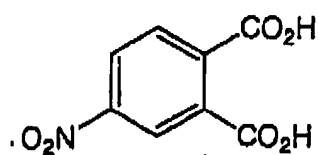


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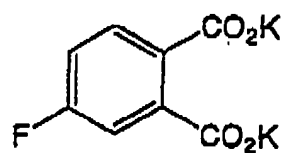
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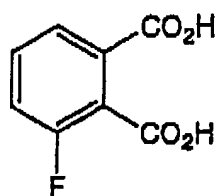
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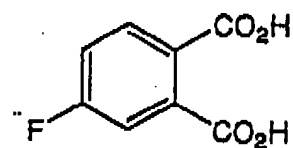
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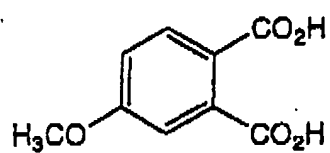
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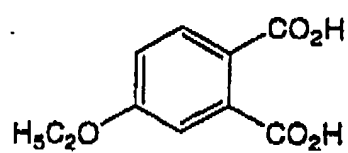
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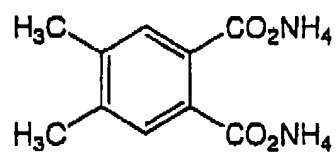
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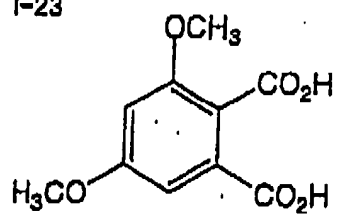


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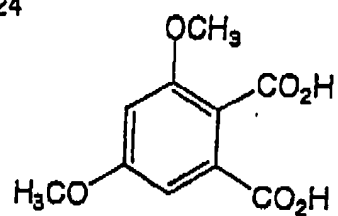


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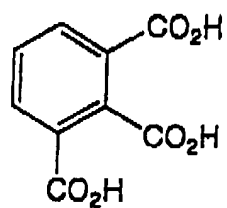
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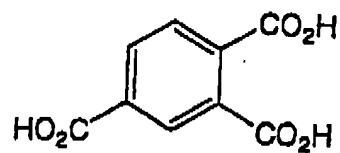
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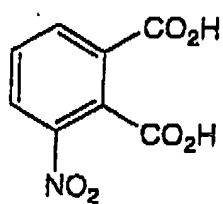
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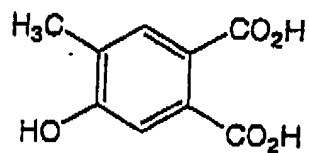
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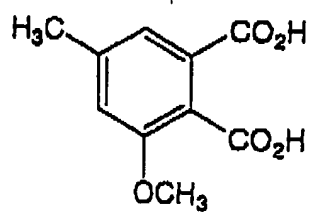
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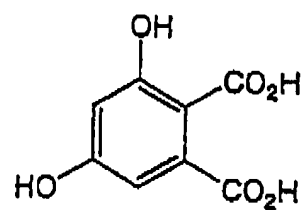
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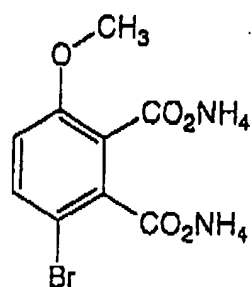


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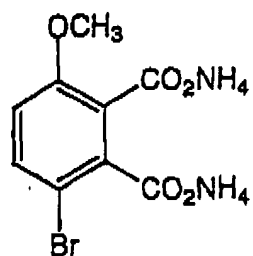


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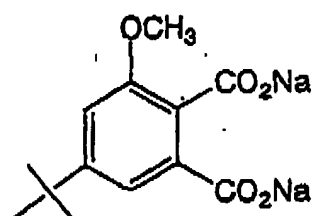
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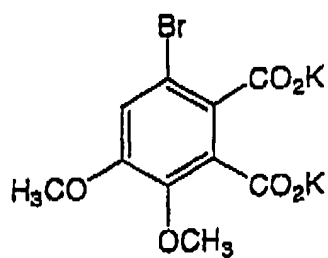
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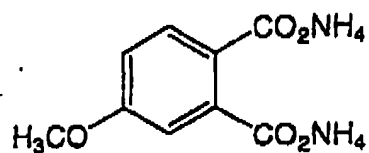
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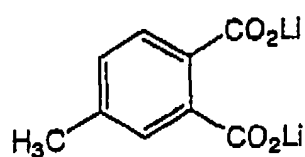
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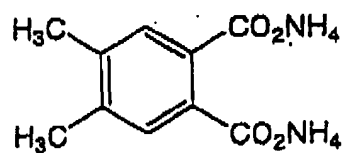
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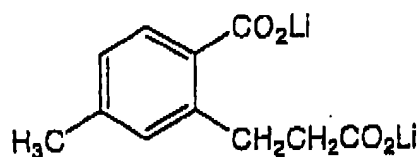


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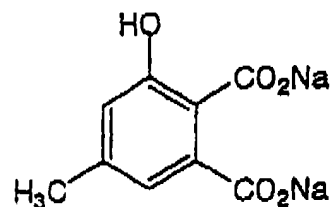


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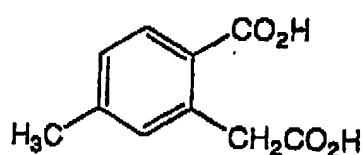
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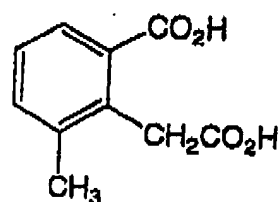
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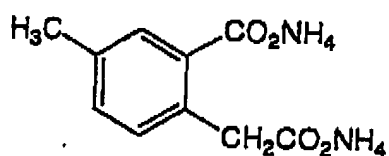
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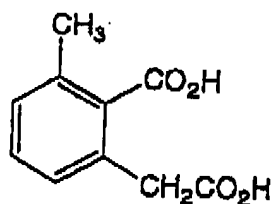
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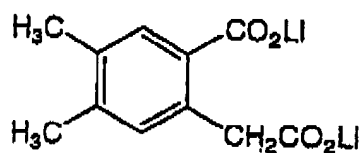
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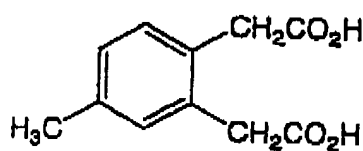
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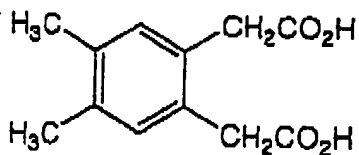
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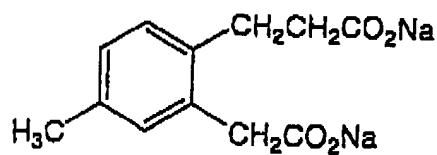
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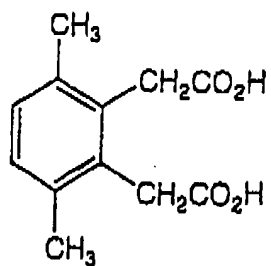


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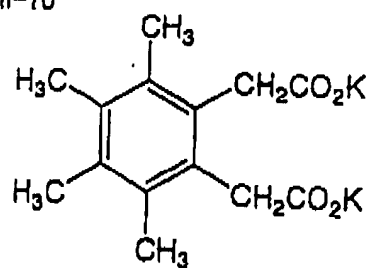


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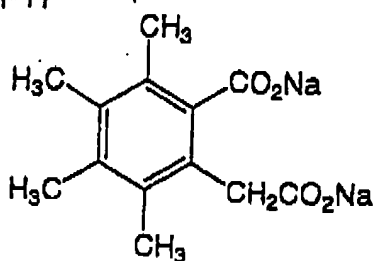
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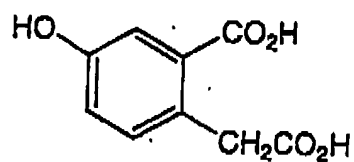
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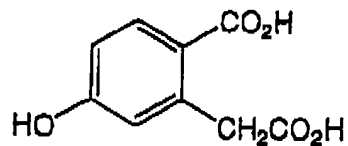
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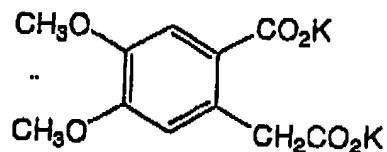
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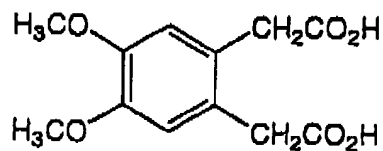
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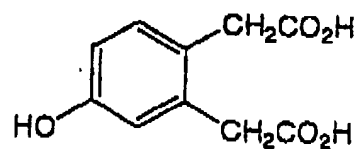
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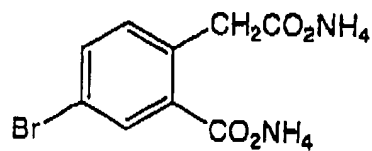
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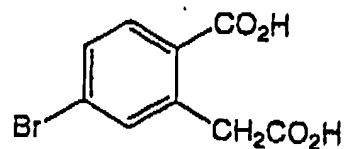
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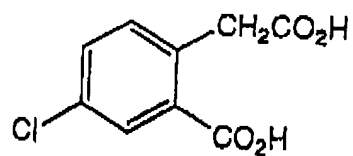


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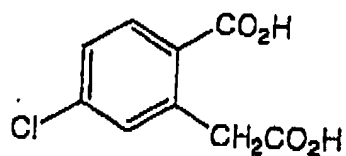


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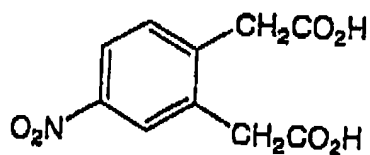
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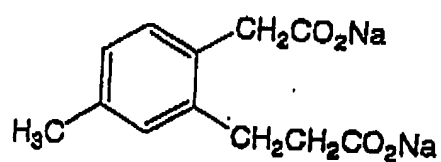
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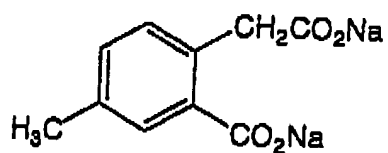
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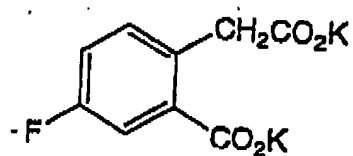
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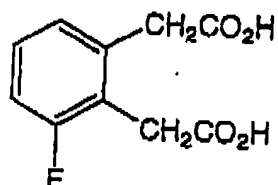
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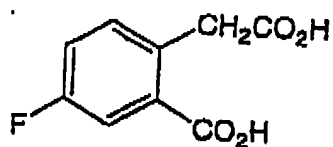
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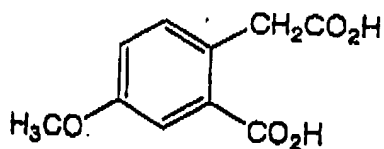
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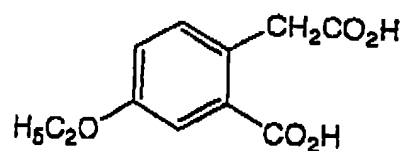
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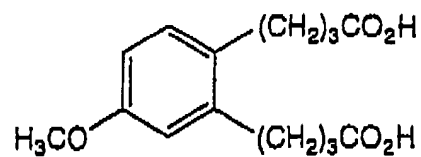


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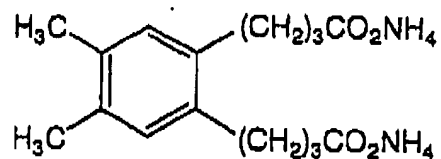


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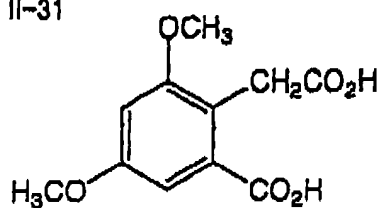
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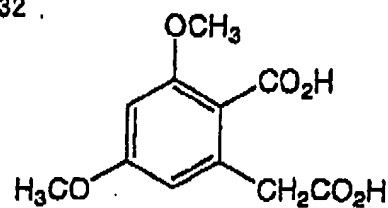
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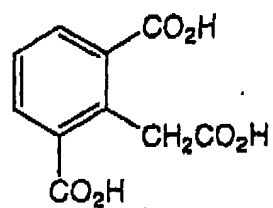
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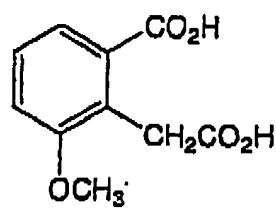
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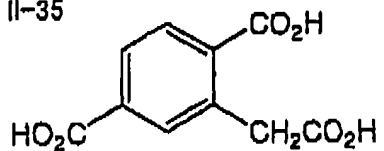
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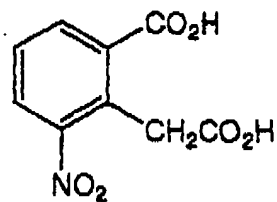
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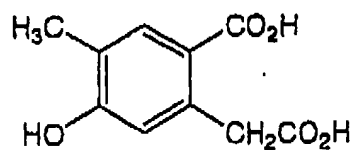
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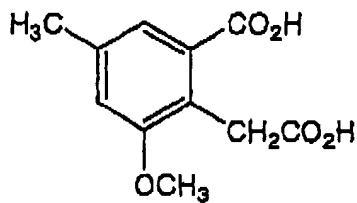
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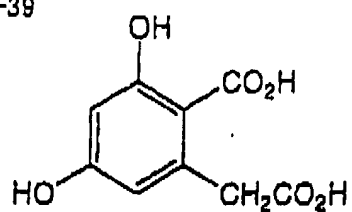


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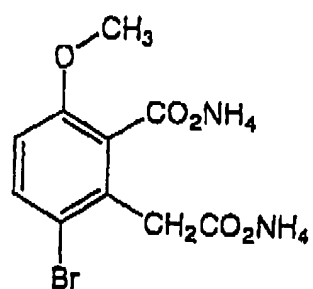


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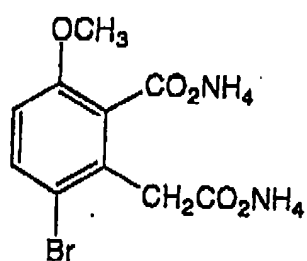
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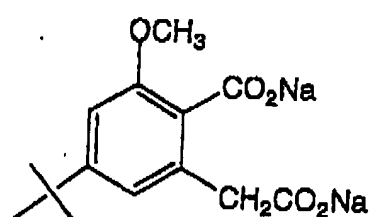
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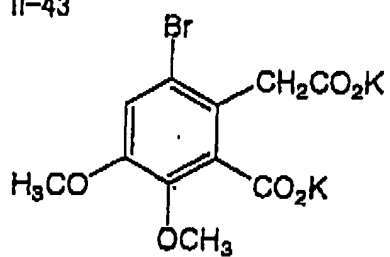
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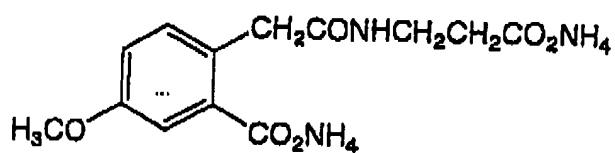
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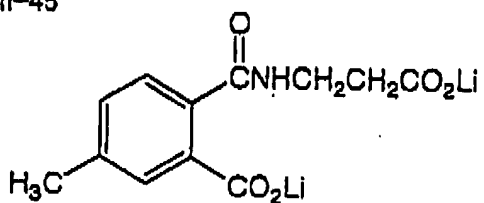
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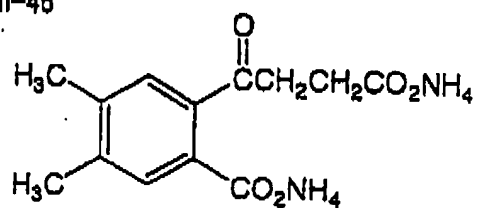
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II-45

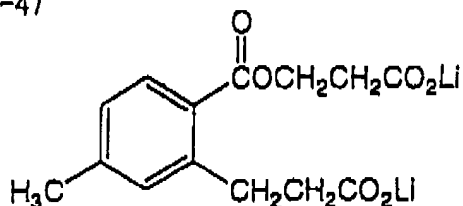


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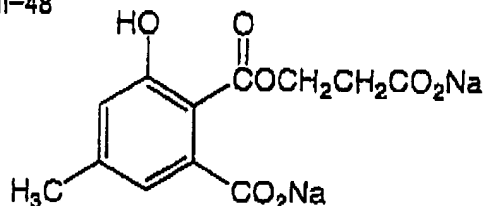


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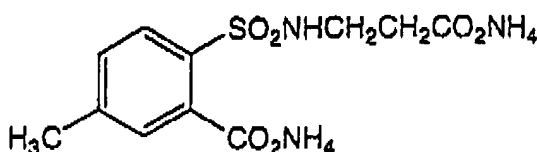
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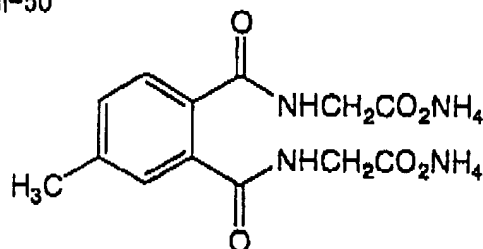
II-48



II-49



II-50



[0066] The compound represented by formula (I) in the present invention can be synthesized according to the methods described in *Tetrahedron*, Vol. 31 (20), pp. 2807 to 2819, *Angewante Chem.*, Vol. 86(9), p. 349 (1974), and the methods in the literature cited therein. Commercially available products are also applicable. The addition amount of the compound represented by formula (I) is preferably from 10^{-3} to 10 mol, more preferably from 10^{-2} to 1 mol per mol of Ag. The compound represented by formula (I) may be used alone or in combination of two or more.

[0067] The compound represented by formula (I) may be added to any layer provided on the same side of the support as the layer containing an organic acid silver salt, e.g., an organic acid silver salt-containing layer (an image-recording layer), a photosensitive layer, an interlayer, and a protective layer, preferably added to an interlayer or a protective layer.

[0068] The compound represented by formula (I) according to the present invention may be added in any form, e.g., a solution, a powder, or a solid fine grain dispersion. A solid fine particle dispersion is prepared using well-known atomizing means, e.g., a ball mill, a vibrating ball mill, a sand mill, a colloid mill, a jet mill, a roller mill, etc. Dispersing aids may be used for solid fine particle dispersion.

[0069] A photothermographic photosensitive material according to the present invention preferably comprises a photosensitive layer containing a photosensitive silver halide (a catalytically active amount of a photocatalyst) and a photo-insensitive layer. The photosensitive layer preferably contains a binder (in general, a synthetic polymer) and a salty organic acid silver salt of the present invention. Further, the photosensitive layer preferably contains a hydrazine compound (a super high contrasting agent) and a tone adjuster (for controlling silver tone). The photosensitive layer may comprise a plurality of layers. For example, the photothermographic photosensitive material may be provided with a high speed-photosensitive layer and a low speed-photosensitive layer with a view to adjusting gradation. The order of the arrangement of the high speed-photosensitive layer and the low speed-photosensitive layer is such that the low speed-photosensitive layer may be arranged at the lower side (nearer to the support) or the high speed-photosensitive layer may be arranged at the lower side.

[0070] In addition to a layer containing a dye, i.e., a filter layer, and an antihalation layer, the photo-insensitive layer may be provided with other functional layer such as a surface protective layer.

[0071] As a support for the photothermographic photosensitive material according to the present invention, paper, polyethylene-coated paper, polypropylene-coated paper, parchment, cloth, a sheet or a thin film of a metal (e.g., aluminum, copper, magnesium, zinc), glass, and glass or plastic films coated with a metal (e.g., a chromium alloy, steel, silver, gold, platinum) can be used. Transparent plastic films are preferably used as a support, and examples of preferred plastics include polyalkyl methacrylate (e.g., polymethyl methacrylate), polyester (e.g., polyethylene terephthalate (PET)), polyvinyl acetal, polyamide (e.g., nylon), and cellulose ester (e.g., cellulose nitrate, cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate). A support preferably has a thickness of from 90 to 190 μm , more preferably from 150 to 185 μm .

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[0072] A support may be covered with a polymer. Examples of polymers which can be used include polyvinylidene chloride, acrylic acid polymers (e.g., polyacrylonitrile, methyl acrylate), polymers of unsaturated dicarboxylic acid (e.g., itaconic acid, acrylic acid), carboxymethyl cellulose and polyacrylamide. Copolymers may also be used. An under-coating layer containing a polymer may be provided in place of being covered with a polymer.

[0073] The silver halide for use in the present invention is not limited in particular and any of silver bromide, silver iodide, silver chloride, silver chlorobromide, silver iodobromide, and silver chlorodibromide can be used in the present invention. The distribution of the halogen composition in the grain may be uniform, the halogen composition may be changed stepwise or may be continuously changed. Silver halide grains having a core/shell structure can be preferably used. Grain structures are preferably from a double structure to a quintuple structure. Core/shell grains having a double structure to a quadruple structure can be more preferably used. Techniques of localizing silver bromide on the surface of silver chloride or silver chlorobromide grains can preferably be used.

[0074] The grain size of the silver halide grain is from 0.001 to 0.04 μm , preferably from 0.005 to 0.04 μm . The equivalent-circle diameters obtained with an electron microscope from the projected areas of the grains are averaged, which is taken as the grain diameter of the silver halide grain in the present invention.

[0075] The addition amount of the silver halide is preferably from 0.03 to 0.6 g/m^2 , more preferably from 0.05 to 0.4 g/m^2 , and most preferably from 0.1 to 0.4 g/m^2 , as the coating amount per m^2 of the photothermographic material.

[0076] The photosensitive silver halide for use in the present invention can be produced using the methods well-known in this industry, for example, the methods disclosed in Research Disclosure, No. 17029 (June, 1978) and U.S. Patent 3,700,458 can be used. Specifically, silver halide is produced as a silver halide emulsion by the reaction of silver nitrate and a soluble halide. Silver halide may be produced by reacting a silver soap with a halogen ion, and converting the soap part of the silver soap to halogen. Alternatively, a halogen ion may be added during a silver soap-forming step.

[0077] Silver halide is generally spectrally sensitized before use. Spectral sensitizing dyes are disclosed in JP-A-60-140335, JP-A-63-159841, JP-A-63-231437, JP-A-63-259851, JP-A-63-304242, JP-A-63-15245, U.S. Patents 4,839,414, 4,740,455, 4,741,966, 4,751,175, and 4,835,096.

[0078] The photosensitive layer and the photo-insensitive layer preferably contain a binder. In general, a colorless and transparent or translucent polymer is used as a binder.

[0079] The effect of the present invention increases when the photosensitive layer is formed by coating a coating solution in which 30% by weight or more of the solvent is occupied by water, and then drying, further, when a polymer latex, which is soluble or dispersible in a water system solvent (water solvent), in particular, having an equilibrium moisture content at 25°C 60% RH of 2% by weight or less, is used as the main binder of the photosensitive layer (70% by weight or more, preferably 80% by weight or more of the total binder of the photosensitive layer). The most preferred polymer of the present invention is a polymer so prepared that ionic conductivity becomes 2.5 mS/cm or less. Such a polymer can be produced by a method of subjecting the polymer synthesized to purifying treatment using a separating function film.

[0080] "A water system solvent" in which the main binder (hereinafter referred to as "the polymer according to the present invention") of the photosensitive layer of the present invention is soluble or dispersible as used herein is water or water mixed with a water-miscible organic solvent in concentration of 70 wt% or less. As water-miscible organic solvents, alcohols such as methyl alcohol, ethyl alcohol, and propyl alcohol, cellosolves such as methyl cellosolve, ethyl cellosolve, and butyl cellosolve, ethyl acetate and dimethylformamide can be exemplified.

[0081] The system of a so-called dispersing state in which a polymer is not dissolved thermodynamically is also called a water system solvent in the present invention.

[0082] "An equilibrium moisture content at 25°C 60% RH" used in the present invention can be represented as follows with the weight of the polymer in humidity condition equilibrium at 25°C 60% RH being W_1 and the weight of the polymer at 25°C dry state being W_0 :

An equilibrium moisture content at 25°C 60% RH =

$$[(W_1 - W_0)/W_0] \times 100 \text{ (wt\%)}$$

[0083] As for the definition and the measuring method of a moisture content, e.g., Polymer Engineering, Lecture 14, "Test Method of Polymeric Materials", compiled by Kobunshi-Gakkai, published by Chijin Shokan Co. Ltd. can be referred to.

[0084] The equilibrium moisture content at 25°C 60% RH of the polymer according to the present invention is preferably 2 wt% or less, more preferably from 0.01 to 1.5 wt%, and still more preferably from 0.02 to 1 wt%.

[0085] The polymers according to the present invention are not particularly restricted so long as they are soluble or dispersible in the above-described water system solvent and have equilibrium moisture content at 25°C 60% RH of 2 wt% or less. Of these polymers, polymers which are dispersible in a water system solvent are particularly preferred.

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[0086] As examples of dispersion conditions, there are latexes in which fine particles of solid polymers are dispersed and dispersions in which polymer molecules are dispersed in a molecular state or with forming micelle, and any of these can be preferably used.

[0087] Hydrophobic polymers such as an acrylic resin, a polyester resin, a rubber-based resin (e.g., an SBR resin), a polyurethane resin, a vinyl chloride resin, a vinyl acetate resin, a vinylidene chloride resin, and a polyolefin resin can be preferably used. Polymers may be straight chain, branched or crosslinked polymers. As polymers, any of homopolymers in which single monomers are polymerized and copolymers in which two or more monomers are copolymerized can be used. When copolymers are used, any of random copolymers and block copolymers can be used. The molecular weight of polymers is from 5,000 to 1,000,000, preferably from 10,000 to 200,000, in number average molecular weight. If the molecular weight is too small, the mechanical strength of the emulsion layer is insufficient, while when it is too large, the film-forming property is disadvantageously deteriorated.

[0088] The polymers according to the present invention comprise the foregoing polymers dispersed in a water system dispersion medium. "Water system dispersion medium" used herein means a dispersion medium in which 30 wt% or more of the composition is occupied by water. As dispersion conditions, any of emulsified dispersion, micell dispersion, dispersion in which polymers having hydrophilic parts in the molecule are dispersed in a molecular state can be used but latexes are particularly preferably used.

[0089] Specific examples of preferred polymers are shown below. In the following, polymers are indicated as raw material monomers, the numerical values in parentheses are wt% and the molecular weights are number average molecular weights.

- P-1: Latex comprising MMA (70)-EA (27)-MAA (3) (molecular weight: 37,000)
- P-2: Latex comprising MMA (70)-2EHA (20)-St (5)-AA (5) (molecular weight: 40,000)
- P-3: Latex comprising St (50)-Bu (47)-MAA (3) (molecular weight: 45,000)
- P-4: Latex comprising St (68)-Bu (29)-AA (3) (molecular weight: 60,000)
- P-5: Latex comprising St (70)-Bu (27)-IA (3) (molecular weight: 120,000)
- P-6: Latex comprising St (75)-Bu (24)-AA (1) (molecular weight: 108,000)
- P-7: Latex comprising St (80)-Bu (35)-DVB (3)-MAA (2) (molecular weight: 150,000)
- P-8: Latex comprising St (70)-Bu (25)-DVB (2)-AA (3) (molecular weight: 280,000)
- P-9: Latex comprising VC (50)-MMA (20)-EA (20)-AN (5)-AA (5) (molecular weight: 80,000)
- P-10: Latex comprising VDC (85)-MMA (5)-EA (5)-MAA (5) (molecular weight: 67,000)
- P-11: Latex comprising Et (90)-MAA (10) (molecular weight: 12,000)
- P-12: Latex comprising St (70)-2EHA (27)-AA (3) (molecular weight: 130,000)
- P-13: Latex comprising MMA (63)-EA (35)-AA (2) (molecular weight: 33,000)

[0090] Abbreviations in the above show the following monomers. MMA: methyl methacrylate, EA: ethyl acrylate, MAA: methacrylic acid, 2EHA: 2-ethylhexyl acrylate, St: styrene, Bu: butadiene, AA: acrylic acid, DVB: divinylbenzene, VC: vinyl chloride, AN: acrylonitrile, VDC: vinylidene chloride, Et: ethylene, and IA: itaconic acid.

[0091] The above-described polymers are commercially available and the following polymers can be used. As examples of acrylic resins, Seblan A-4635, 46583, and 4601 (manufactured by Daicel Chemical Industries Ltd.), Nipol Lx811, 814, 821, 820, and 857 (manufactured by Nippon Zeon Co., Ltd.), as examples of polyester resins, FINETEX ES650, 611, 675, and 850 (manufactured by Dainippon Chemicals and Ink Co., Ltd.), WD-size and WMS (manufactured by Eastman Chemical Co.), as examples of polyurethane resins, HYDRAN AP10, 20, 30, and 40 (manufactured by Dainippon Chemicals and Ink Co., Ltd.), as examples of rubber-based resins, LACSTAR 7310K, 3307B, 4700H, and 7132C (manufactured by Dainippon Chemicals and Ink Co., Ltd.), Nipol Lx416, 410, 438C, and 2507 (manufactured by Nippon Zeon Co., Ltd.), as examples of vinyl chloride resins, G351 and G576 (manufactured by Nippon Zeon Co., Ltd.), as examples of vinylidene chloride resins, L502 and L513 (manufactured by Asahi Chemical Industry Co., Ltd.), and as examples of olefin resins, Chempearl S120 and SA100 (manufactured by Mitsui Petrochemical Industries, Ltd.) can be exemplified.

[0092] These polymers may be used alone as polymer latexes or two or more polymers may be blended, if necessary.

[0093] Styrene/butadiene copolymer latexes are particularly preferably used in the present invention. The weight ratio of the styrene monomer unit and the butadiene monomer unit in styrene/butadiene copolymers is preferably from 40/60 to 95/5. The ratio occupied by the styrene monomer unit and the butadiene monomer unit in the copolymer is preferably from 80 to 99 wt%. The preferred molecular weight is the same as described above.

[0094] Preferred styrene/butadiene copolymer latexes which can be used in the present invention are the foregoing P-3 and P-8 and commercially available products LACSTAR-3307B, 7132C, and Nipol Lx416.

[0095] Hydrophilic polymers such as gelatin, polyvinyl alcohol, methyl cellulose, and hydroxypropyl cellulose may be added to the photosensitive layer of the present invention, according to necessity. The addition amount of these hydrophilic polymers is preferably 30 wt% or less, more preferably 20 wt% or less, based

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on the total amount of the binder of the photosensitive layer.

[0096] The photosensitive layer according to the present invention is preferably formed of polymer latexes. The weight ratio of the total binder/the organic silver salt in the photosensitive layer is preferably from 1/10 to 10/1, more preferably from 1/5 to 4/1.

[0097] The weight ratio of the total binder/silver halide is preferably from 400 to 5, more preferably from 200 to 10.

[0098] The total amount of the binder in the photosensitive layer of the present invention is preferably from 0.2 to 30 g/m², more preferably from 1 to 15 g/m². The photosensitive layer of the present invention may contain a crosslinking agent for crosslinking and a surfactant for improving coating property.

[0099] The solvent for the coating solution of the photosensitive layer of the photosensitive material of the present invention (solvent and dispersion medium are briefly expressed as solvent collectively) is a water system solvent containing 30 wt% or more of water. As components other than water, water-miscible organic solvents such as methyl alcohol, ethyl alcohol, isopropyl alcohol, methyl cellosolve, ethyl cellosolve, dimethylformamide and ethyl acetate may be arbitrarily used in the coating solution. The water content in the solvent of the coating solution is preferably 50% by weight or more, more preferably 70% by weight or more. Preferred examples of the compositions of the solvent include, in addition to water, water/methyl alcohol = 90/10 (wt%), water/methyl alcohol = 70/30, water/methyl alcohol/ dimethylformamide = 80/15/5, water/methyl alcohol/ethyl cellosolve = 85/10/5, water/methyl alcohol/isopropyl alcohol = 85/10/5, etc.

[0100] It is preferred for the photosensitive layer or the photo-insensitive layer to further contain a super high contrasting agent. When the photothermographic (photosensitive) material is used in the field of a photograph for printing, the reproduction of a continuous gradation image by dots and a line image is important. The reproduction of a dot image and a line image can be removed by using a super high contrast-increasing agent. As a super high contrast-increasing agent, hydrazine compounds, quaternary ammonium compounds or acrylonitrile compounds (e.g., disclosed in U.S. Patent 5,545,515) can be used. Hydrazine compounds are particularly preferably used.

[0101] Hydrazine compounds include a compound in which hydrazine (H₂N-NH₂) and at least one of hydrogen atoms are substituted. As the substituent, an aliphatic, aromatic or heterocyclic group is directly bonded to the nitrogen atom of the hydrazine, or an aliphatic, aromatic or heterocyclic group is bonded to the nitrogen atom of the hydrazine via a linking group. Examples of the linking groups include -CO-, -CS-, -SO₂-, -POR- (R represents an aliphatic, aromatic or heterocyclic group), -CNH- and combinations of these.

[0102] Hydrazine compounds are disclosed in U.S. Patents 5,464,798, 5,498,695, 5,512,411, 5,538,622, JP-B-8-77138 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-B-6-93082, JP-A-6-230497, JP-A-6-289520, JP-A-6-313951, JP-A-7-5610, JP-A-7-77783, and JP-A-7-104426.

[0103] A hydrazine compound can be dissolved in an appropriate organic solvent and then added to a coating solution for a photosensitive layer. Examples of organic solvents include alcohols (e.g., methanol, ethanol, propanol, fluorinated alcohol), ketones (e.g., acetone, methyl ethyl ketone), dimethylformamide, dimethyl sulfoxide, and methyl cellosolve. A hydrazine compound may be dissolved in an oily (auxiliary) solvent and the solution may be emulsified in a coating solution. Examples of oily (auxiliary) solvents include dibutyl phthalate, tricresyl phosphate, glyceryl triacetate, diethyl phthalate, ethyl acetate and cyclohexanone. Further, a solid dispersion of a hydrazine compound may be added to a coating solution. Dispersion of a hydrazine compound can be performed using well-known dispersing machines such as a ball mill, a colloid mill, Manton Gauling, microfluidizer, or an ultrasonic disperser.

[0104] The addition amount of a super high contrasting agent is preferably from 1×10⁻⁶ to 1×10⁻² mol, more preferably from 1×10⁻⁵ to 5×10⁻³ mol, and most preferably from 2×10⁻⁶ to 5×10⁻³ mol, per mol of the silver halide.

[0105] In addition to a super high contrast-increasing agent, a high contrast accelerating agent may be used in the present invention. Examples of high contrast accelerating agents include an amine compound (e.g., disclosed in U.S. Patent 5,545,506), a hydroxamic acid (e.g., disclosed in U.S. Patent 5,545,507), acrylonitriles (e.g., disclosed in U.S. Patent 5,545,507), and a hydrazine compound (e.g., disclosed in U.S. Patent 5,558,983).

[0106] It is preferred for a photosensitive layer or a photo-insensitive layer to contain a tone adjusting agent (a toner). A tone adjusting agent is described in Research Disclosure, No. 17029.

[0107] Examples of tone adjusting agents include imides (e.g., phthalimide); cyclic imides (e.g., succinimide); pyrazolin-5-ones (e.g., 3-phenyl-2-pyrazolin-5-one, 1-phenylurazol); quinoxalones (e.g., quinoxaline, 2,4-thiazolidinedione); naphthalimides (e.g., N-hydroxy-1,8-naphthalimide); cobalt complexes (e.g., cobalt hexamethylenetrifluoroacetate); mercaptans (e.g., 3-mercapto-1,2,4-triazole); N-(aminomethyl)aryldicarboxyimides (e.g., N-(dimethylaminomethyl)phthalimide); blocked pyrazoles (e.g., N,N'-hexamethylene-1-carbamoyl-3,5-dimethylpyrazole); combinations of isothluronium derivatives (e.g., 1,8-(3,6-dioxaoctane)bis(isothluroniumtrifluoroacetate) with photo-bleaching agent (e.g., 2-tribromomethylsulfonyl)benzothiazole); merocyanine dyes (e.g., 3-ethyl-5-[(3-ethyl-2-benzothiazolynilidene)-1-methylethylidene]-2-thio-2,4-oxazolidinedione); phthalazirone compounds and metal salts thereof (e.g., phthalazirone, 4-(1-naphthyl)phthalazirone, 6-chlorophthalazirone, 5,7-dimethoxyphthalazirone, 2,3-dihydro-1,4-phthalazinedione, 8-methylphthalazine); combinations of phthalazirone compounds and sulfinic acid derivatives (e.g., sodium benzenesulfinate); combinations of phthalazirone compounds and sulfonic acid derivatives (e.g., sodium p-toluenesul-

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ionate); phthalazine and derivatives thereof (e.g., phthalazine, 6-isopropylphthalazine, 6-methylphthalazine); combinations of phthalazines and phthalic acids; combinations of phthalazines or phthalazine adducts with dicarboxylic acids (e.g., preferably-phenylsuccinic acid) or anhydrides thereof (e.g., maleic anhydride, phthalic acid, 2,3-naphthalenedicarboxylic acid, phthalic anhydride, 4-methylphthalic acid, 4-nitrophthalic acid, tetrachlorophthalic anhydride); quinazolin-
 ediones; benzoxazine; naphthooxazine derivatives; benzoxazine-2,4-diones (e.g., 1,3-benzoxazine-2,4-dione); pyrimidines, asymmetric triazines (e.g., 2,4-dihydroxypyrimidine); tetraazapentalene derivatives (e.g., 3,6-dimercapto-1,4-diphenyl-1H,4H-2,3a,5,6a-tetraazapentalene). Of these compounds, phthalazines are particularly preferred.

[0108] Tone adjusting agents are preferably contained in the surface of a photosensitive layer in an amount of from 0.1 to 50 mol%, more preferably from 0.5 to 20 mol%, per mol of the silver.

[0109] An antifoggant may be added to a photosensitive layer or a photo-insensitive layer (preferably a photosensitive layer). As antifoggants, non-mercury compounds (e.g., those disclosed in U.S. Patents 3,874,946, 4,548,075, 4,452,885, 4,758,999, 5,028,523, British Patent Application Nos. 92,221,383.4, 9,300,147.7, 9,311,790.1, and JP-A-59-57234) are preferably used in the present invention rather than mercury compounds (e.g., disclosed in U.S. Patent 3,589,903).

[0110] Particularly preferred antifoggants are heterocyclic compounds having a halogen (e.g., F, Cl, Br, I)-substituted methyl group.

[0111] It is preferred to use polyvinyl alcohol (PVA) in the photothermographic material, in particular, the protective layer of photothermographic (photosensitive) material, according to the present invention. Examples of PVA which can be used in the present invention are shown below.

Examples of Completely Saponified Products

[0112]

PVA-105 [polyvinyl alcohol (PVA) content: 94.0 wt% or more, saponification degree: 98.5 \pm 0.5 mol%, sodium acetate content: 1.5 wt% or less, volatile content: 5.0 wt% or less, viscosity (4 wt%, 20°C): 5.6 \pm 0.4 CPS].

PVA-110 [PVA content: 94.0 wt%, saponification degree: 98.5 \pm 0.5 mol%, sodium acetate content: 1.5 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 11.0 \pm 0.8 CPS].

PVA-117 [PVA content: 94.0 wt%, saponification degree: 98.5 \pm 0.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 28.0 \pm 3.0 CPS].

PVA-117H [PVA content: 93.5 wt%, saponification degree: 99.6 \pm 0.3 mol%, sodium acetate content: 1.85 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 29.0 \pm 3.0 CPS].

PVA-120 [PVA content: 94.0 wt%, saponification degree: 98.5 \pm 0.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 39.5 \pm 4.5 CPS].

PVA-124 [PVA content: 94.0 wt%, saponification degree: 98.5 \pm 0.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 60.0 \pm 6.0 CPS].

PVA-124H [PVA content: 93.5 wt%, saponification degree: 99.6 \pm 0.3 mol%, sodium acetate content: 1.85 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 61.0 \pm 6.0 CPS].

PVA-CS [PVA content: 94.0 wt%, saponification degree: 97.5 \pm 0.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 27.5 \pm 3.0 CPS].

PVA-CST [PVA content: 94.0 wt%, saponification degree: 96.0 \pm 0.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 27.0 \pm 3.0 CPS].

PVA-HC [PVA content: 90.0 wt%, saponification degree: 99.85 mol% or more, sodium acetate content: 2.5 wt%, volatile content: 8.5 wt%, viscosity (4 wt%, 20°C): 25.0 \pm 3.5 CPS], etc. (All of the above products are manufactured by Kuraray Co., Ltd.)

Examples of Partially Saponified Products

[0113]

PVA-203 [PVA content: 94.0 wt%, saponification degree: 88.0 \pm 1.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 3.4 \pm 0.2 CPS].

PVA-204 [PVA content: 94.0 wt%, saponification degree: 88.0 \pm 1.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 3.9 \pm 0.3 CPS].

PVA-205 [PVA content: 94.0 wt%, saponification degree: 88.0 \pm 1.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 5.0 \pm 0.4 CPS].

PVA-210 [PVA content: 94.0 wt%, saponification degree: 88.0 \pm 1.0 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 9.0 \pm 1.0 CPS].

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PVA-217 [PVA content: 94.0 wt%, saponification degree: 88.0 ± 1.0 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 22.5 ± 2.0 CPS].

PVA-220 [PVA content: 94.0 wt%, saponification degree: 88.0 ± 1.0 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 30.0 ± 3.0 CPS].

5 PVA-224 [PVA content: 94.0 wt%, saponification degree: 88.0 ± 1.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 44.0 ± 4.0 CPS].

PVA-228 [PVA content: 94.0 wt%, saponification degree: 88.0 ± 1.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 65.0 ± 5.0 CPS].

10 PVA-235 [PVA content: 94.0 wt%, saponification degree: 88.0 ± 1.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 95.0 ± 15.0 CPS].

PVA-217EE [PVA content: 94.0 wt%, saponification degree: 88.0 ± 1.0 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 23.0 ± 3.0 CPS].

PVA-217E [PVA content: 94.0 wt%, saponification degree: 88.0 ± 1.0 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 23.0 ± 3.0 CPS].

15 PVA-220E [PVA content: 94.0 wt%, saponification degree: 88.0 ± 1.0 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 31.0 ± 4.0 CPS].

PVA-224E [PVA content: 94.0 wt%, saponification degree: 88.0 ± 1.0 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 45.0 ± 5.0 CPS].

20 PVA-403 [PVA content: 94.0 wt%, saponification degree: 80.0 ± 1.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 3.1 ± 0.3 CPS].

PVA-405 [PVA content: 94.0 wt%, saponification degree: 81.5 ± 1.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 4.8 ± 0.4 CPS].

PVA-420 [PVA content: 94.0 wt%, saponification degree: 79.5 ± 1.5 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%].

25 PVA-613 [PVA content: 94.0 wt%, saponification degree: 93.5 ± 1.0 mol%, sodium acetate content: 1.0 wt%, volatile content: 5.0 wt%, viscosity (4 wt%, 20°C): 18.5 ± 2.0 CPS].

L-8 [PVA content: 96.0 wt%, saponification degree: 71.0 ± 1.5 mol%, sodium acetate content: 1.0 wt% (ash content), volatile content:

30 3.0 wt%, viscosity (4 wt%, 20°C): 5.4 ± 0.4 CPS], etc. (All of the above products are manufactured by Kuraray Co., Ltd.)

[0114] The above measured values are obtained according to JIS K-6728-1977.

[0115] Modified polyvinyl alcohols described in Koichi Nagano et al., Pova, published by Kobunshi-kankokai can be used in the present invention. Those modified with a cation, an anion, an -SH compound, an alkylthio compound and a silanol compound can be used.

[0116] There can be exemplified as modified polyvinyl alcohol (modified PVA), as C polymer, C-118, C-318, C-318-2A, and C-506 (manufactured by Kuraray Co., Ltd.).

As HL polymer, HL-12E, HL-1203 (manufactured by Kuraray Co., Ltd.).

40 As HM polymer, HM-03 and HM-N-03 (manufactured by Kuraray Co., Ltd.).

As K polymer, KL-118, KL-318, KL-508, KM-118T and KM-618 (manufactured by Kuraray Co., Ltd.).

As M polymer, M-115 (manufactured by Kuraray Co., Ltd.).

As MP polymer, MP-102, MP-202, and MP-203 (manufactured by Kuraray Co., Ltd.).

As R polymer, R-1130, R-2105 and R-2130 (manufactured by Kuraray Co., Ltd.).

45 As V polymer, V-2250 (manufactured by Kuraray Co., Ltd.).

[0117] The coating amount of polyvinyl alcohol of the protective layer (per one layer) is preferably from 0.3 to 4.0 g/m², more preferably from 0.3 to 2.0 g/m² per m² of the support.

[0118] The photothermographic material, in particular, the protective layer of the photothermographic (photosensitive) material, according to the present invention preferably contains a matting agent. Matting agents in general comprise fine particles of water-insoluble organic or inorganic compounds. Optional matting agents can be used in the present invention. Organic matting agents disclosed in U.S. Patents 1,939,213, 2,701,245, 2,322,037, 3,262,782, 3,539,944, and 3,767,448, and inorganic matting agents disclosed in U.S. Patents 1,260,772, 2,192,241, 3,257,208, 3,370,951, 3,523,022 and 3,769,020 are well-known in this industry and can be used in the present invention. As specific examples of organic compounds which can be used as matting agents, examples of water-dispersible vinyl polymers include polymethyl acrylate, polymethyl methacrylate, polyacrylonitrile, acrylonitrile- α -methylstyrene copolymers, polystyrene, styrene-divinylbenzene copolymers, polyvinyl acetate, polyethylene carbonate, polytetrafluoroethylene, etc., examples of cellulose derivatives include methyl cellulose, cellulose acetate, cellulose acetate propionate,

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etc., examples of starch derivatives include carboxyl starch, carboxynitrophenyl starch, urea-formaldehyde-starch reaction products, etc., hardened gelatin treated with well-known hardening agents and hardened gelatin as microencapsulated hollow particles by coacervation hardening can be preferably used. As examples of inorganic compounds, silicon dioxide, titanium dioxide, magnesium dioxide, aluminum oxide, barium sulfate, calcium carbonate, silver chloride and silver bromide desensitized by a well-known method, glass, and diatomaceous earth can be preferably used. These matting agents can be mixed with different kinds of substances, if necessary.

[0119] In the present invention, matting agents having a particle size of from 2 to 6 μm can be preferably used. The particle size distribution of the matting agent may be broad or narrow. On the other hand, as matting agents largely affect the haze of the photosensitive material and the surface gloss, it is desired to adjust particle size, particle shape and particle size distribution to a necessary condition when matting agents are prepared or by mixing a plurality of matting agents.

[0120] The equivalent-circle diameters obtained with an electron microscope from the projected areas of the particles are averaged, which is taken as the particle diameter of the matting agent in the present invention.

[0121] The coating amount of the matting agent is from 1 to 400 mg/m^2 , more preferably from 5 to 300 mg/m^2 , and it is particularly preferred that the coating amount of the matting agent having a particle size of 4 μm or more is from 5 to 150 mg/m^2 .

[0122] When a matting agent is contained in the layer on the surface side of an image-recording layer or a photosensitive layer, a protective layer is optimal. A protective layer may comprise two layers, if necessary. By selecting the layers to contain an additive, a film pH adjusting agent, an electrostatic charge adjusting agent, an ultraviolet absorber, a sliding agent and a surfactant which participate in development, it is possible to design so as to reconcile a coating property and production suitability with image performance. It is preferred for the outermost protective layer to contain a fluorine-based surfactant together with a matting agent. As fluorine-based surfactants, fluorine-based high molecular surfactants disclosed in JP-A-62-170950 and U.S. Patent 5,380,844, fluorine-based surfactants disclosed in JP-A-60-244945 and JP-A-63-188135 can be exemplified.

[0123] In the present invention, it is preferred that a matting agent is contained in the outermost protective layer.

[0124] A matting agent may be contained in a backing layer, and in this case the layer to contain a matting agent is preferably not the outermost layer on the back surface side.

[0125] A hardening agent may be used in each of an image-recording layer (preferably a photosensitive layer), a protective layer, and a backing layer. Examples of hardening agents are described in T.H. James, The Theory of the Photographic Process, the 4th Ed., pp. 77 to 87, Macmillan Publishing Co., Inc. (1977), and polyvalent metal ions described on p. 78 of the above literature, polyisocyanates disclosed in U.S. Patent 4,281,060 and JP-A-6-208183, epoxy compounds disclosed in U.S. Patent 4,791,042, and vinyl sulfone compounds disclosed in JP-A-62-69048 are preferably used in the present invention.

[0126] Any adhesion preventing material may be used as the surface protective layer according to the present invention. Examples of adhesion preventing materials include waxes, silica particles, styrene-containing elastomeric block copolymers (e.g., styrene-butadiene-styrene, styrene-isoprene-styrene), cellulose acetate, cellulose acetate butyrate, cellulose propionate, and mixtures of these. Further, the surface protective layer of the present invention may contain a crosslinking agent for crosslinking and a surfactant for improving a coating property.

[0127] The image-recording layer or the protective layer of the image-recording layer according to the present invention can contain light absorbing substances or filter dyes as disclosed in U.S. Patents 3,253,921, 2,274,782, 2,527,583 and 2,956,879. Further, dyes can be mordanted as disclosed in U.S. Patent 3,282,699.

[0128] The image-recording layer or the protective layer of the image-recording layer according to the present invention can contain a matting agent, e.g., starch, titanium dioxide, zinc oxide, silica, or polymer beads containing beads disclosed in U.S. Patents 2,992,101 and 2,701,245. The matting degree of the emulsion surface is not particularly limited so long as white-spot unevenness does not occur, but Beck's smoothness is preferably from 200 to 10,000 seconds, particularly preferably from 300 to 10,000 seconds.

[0129] The photothermographic (photosensitive) material according to the present invention is preferably a mono-sheet type material (a type capable of forming an image on the photothermographic (photosensitive) material not using other sheet, e.g., an image-receiving material).

[0130] The photothermographic (photosensitive) material according to the present invention may further contain a surfactant, an antioxidant, a stabilizer, a plasticizer, an ultraviolet absorber, or a coating aid. Various additives are added to either a photosensitive layer or a photo-insensitive layer. With respect to the addition of these additives, WO 98/36322, EP-A-803764, JP-A-10-186567 and JP-A-10-18568 can be referred to.

[0131] The photosensitive layer of the present invention can contain, as a plasticizer and a lubricant, polyhydric alcohols (e.g., glycerins and diols disclosed in U.S. Patent 2,980,404), fatty acids or fatty acid esters disclosed in U.S. Patents 2,588,785 and 3,121,060, and silicone resins disclosed in British Patent 955,061.

[0132] It is preferred in the photothermographic (photosensitive) material of the present invention that the photo-insensitive layer contains a decoloring dye and a base precursor to function as a filter layer or an antihalation layer. A

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photothermographic (photosensitive) material generally has photo-insensitive layers in addition to photosensitive layers. Photo-insensitive layers can be classified from the arrangement to (1) a protective layer provided on a photosensitive layer (farther from a support), (2) an interlayer provided between a plurality of photosensitive layers or between a photosensitive layer and a protective layer, (3) an undercoating layer provided between a photosensitive layer and a support, and (4) a backing layer provided on the opposite side to a photosensitive layer. A filter layer is provided in a photosensitive material as a layer of (1) or (2). An antihalation layer is provided in a photosensitive material as a layer of (3) or (4).

[0133] A decoloring dye and a base precursor are preferably added to the same photo-insensitive layer. They may be added to two adjacent photo-insensitive layers separately. Further, a barrier layer may be provided between two photo-insensitive layers. In the present invention, "a layer contains a decoloring dye and a base precursor" includes the case in which a plurality of adjacent layers contain a decoloring dye and a base precursor separately.

[0134] A decoloring dye can be added to the coating solution of a photo-insensitive layer as a solution, an emulsion, a solid fine particle dispersion, or a polymer impregnated product. A dye can also be added to a photo-insensitive layer using a polymer mordant. These addition methods are the same as the methods employed for adding dyes to general photothermographic (photosensitive) materials. Latexes used in polymer impregnated products are disclosed in U.S. Patent 4,199,363, German Patent Publication Nos. 2,541,274 and 2,541,230, EP 029104, and JP-B-53-41091. With respect to the emulsifying method for adding a dye to a solution containing a dissolved polymer is disclosed in 88/00723.

[0135] The addition amount of a decoloring dye is determined by the purpose of the dye. In general, a decoloring dye is used in the amount giving optical density (absorbance) exceeding 0.1 when measured at objective wavelength. Optical density is preferably from 0.2 to 2. The addition amount of a dye for obtaining such optical density is in general from about 0.001 to about 1 g/m², preferably from about 0.005 to about 0.8 g/m², and particularly preferably from about 0.01 to about 0.2 g/m².

[0136] Decoloration of dyes according to the present invention results in the reduction of optical density to 0.1 or less. Two or more kinds of decoloring dyes may be used in combination in a thermal decoloring type recording material and a photothermographic (photosensitive) material. Two or more kinds of base precursors may also be used in combination.

[0137] The photosensitive material according to the present invention may be provided with an antistatic layer or an electrically conductive layer, e.g., layers containing soluble salts (e.g., chloride, nitrate), metal deposited layers, layers containing ionic polymers disclosed in U.S. Patents 2,861,058 and 3,208,312, and insoluble inorganic salts disclosed in U.S. Patent 3,428,451.

[0138] The method for obtaining a color image with the photothermographic (photosensitive) material according to the present invention is disclosed in JP-A-7-13295, from p. 10, left column, 1. 43 to p. 11, left column, 1. 40. Color dye image stabilizers are disclosed in British Patent 1,326,889, U.S. Patents 3,432,300, 3,698,909, 3,574,627, 3,573,050, 3,764,337 and 4,042,394.

[0139] The photothermographic material, in particular photothermographic (photosensitive) material, according to the present invention may be coated by any method. Specifically, extrusion coating, slide coating, curtain coating, immersion coating, knife coating, flow coating, and various coating methods including extrusion coating using hoppers disclosed in U.S. Patent 2,681,294 can be used. Extrusion coating and slide coating described in Stephen F. Kistler, Peter M. Schwalzer, Liquid Film Coating, pp. 399 to 536, Chapman & Hall Co. (1987) are preferably used, particularly preferably slide coating is used. Examples of the shapes of slide coaters for use in slide coating are described in ibid., p. 427, Figure 11b.1. Two or more layers can be coated simultaneously by the methods described in ibid., pp. 399 to 536, U.S. Patent 2,761,791 and British Patent 837,095, if desired. Simultaneous coating methods are preferably used.

[0140] Surfactants may be used in the present invention for the purpose of improving coating property and electric charge. Any surfactant can be used arbitrarily, e.g., nonionic, anionic, cationic and fluorine-based surfactants. Specifically, fluorine-based high molecular surfactants disclosed in JP-A-62-170950 and U.S. Patent 5,380,644, fluorine-based surfactants disclosed in JP-A-60-244945 and JP-A-63-168135, polysiloxane-based surfactants disclosed in U.S. Patent 3,895,985, and polyalkylene oxide and anionic surfactants disclosed in JP-A-6-301140 can be exemplified.

[0141] In a photothermographic (photosensitive) material, an image is formed by heating after image exposure. A black tone silver image is formed by this heat development. Image exposure is preferably performed with a laser. The heating temperature of the heat development is preferably from 80 to 250°C, more preferably from 100 to 200°C. Heating period of time is generally from 1 second to 2 minutes.

[0142] A plate heater system is preferably used as the heat developing method. Plate heater systems disclosed in JP-A-11-133572 and Japanese Patent Application No. 10-177610 are preferred, which are methods using a heat developing apparatus to obtain a visible image by making a photothermographic (photosensitive) material, in which a latent image has been formed, contact with a heating means at a heat development part. The foregoing heating means comprises a plate heater, and a plurality of pressing rollers are arranged along one surface of the plate heater vis-à-vis with the plate heater. Heat development is performed by passing the foregoing photothermographic (photosensitive) material between the above pressing rollers and the plate heater.

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[0143] As a heating method in heat development process, embodiments shown in Figs. 1 and 2 can be exemplified.

[0144] A photothermographic (photosensitive) material transported to an image exposure part is scanning-exposed by laser beams etc. and transported to heat developing part 18 by means of transporting rollers etc. after a latent image has been formed on the photothermographic (photosensitive) material. During transportation, dusts on the back and front surfaces of the material are removed by a dust removing roller.

[0145] As shown in Fig. 1, heat developing part 18 is a part to make a latent image a visible image by heat development by heating the photothermographic (photosensitive) material. The present invention is characterized in that heat developing part 18 comprises plate heater 120 and a plurality of pressing rollers 122 arranged vis-a-vis with plate heater 120.

[0146] Plate heater 120 is a plate-like heating member encasing a heating unit such as nichrome wire laid down in a planar state, which is maintained at developing temperature of the photothermographic (photosensitive) material. The surface of plate heater 120 is preferably coated with fluororesins or stuck with a fluororesin sheet for the purpose of lessening a friction coefficient or giving abrasion resistance.

[0147] The volatile content of the photothermographic (photosensitive) material is evaporated by heating during heat development, as a result, the photothermographic photosensitive material rises from plate heater 120, and the contact of the photothermographic (photosensitive) material with plate heater 120 sometimes becomes uneven. Therefore, it is also preferred to form minute concavities and convexities on the surface of plate heater 120 to dissipate this vapor.

[0148] It is also preferred to provide temperature gradient so as to make the temperature of both ends of plate heater 120 higher than the temperature of other parts for compensating for the temperature reduction due to heat dissipation at both ends.

[0149] Pressing rollers 122 are arranged with a prescribed pitch being in contact with one surface of plate heater 120 with a distance smaller than the thickness of the photothermographic (photosensitive) material along the entire length of the transporting direction of plate heater 120, and these pressing rollers 122 and plate heater 120 constitute the path of the photothermographic (photosensitive) material. Making the distance of the path of the photothermographic (photosensitive) material smaller than the thickness of the photothermographic (photosensitive) material can prevent the photothermographic (photosensitive) material from buckling. Feeding rollers 126 for feeding the photothermographic (photosensitive) material to heat developing part 18 from the direction of the indicated arrow and discharging rollers 128 for discharging the photothermographic (photosensitive) material to the direction of the indicated arrow after heat development are arranged at both ends of the path of the photothermographic (photosensitive) material.

[0150] Further, it is preferred to provide heat insulating cover 125 for heat insulation on the surface side of pressing rollers 122 opposite to plate heater 120.

[0151] When the photothermographic (photosensitive) material is transported, if the tip of the photothermographic (photosensitive) material strikes against pressing roller 122, the photothermographic (photosensitive) material stops a moment. At that time, if pressing rollers 122 are arranged with the same pitch, the same part of the photothermographic (photosensitive) material stops at every pressing roller 122 and that part of the photothermographic (photosensitive) material is pressed against plate heater 120 for longer time, which sometimes results in generation of streaky uneven development stretching in the width direction. Therefore, it is preferred to make pitch of each pressing roller 122 uneven.

[0152] As shown in Fig. 2, the constitution of heat developing part 18 may also be such that driving roller 130 is arranged in contact with each pressing roller 122 with making the enveloping surface of each pressing roller 122 the circumferential surface and each pressing roller 122 is rotated by the rotation of driving roller 130.

[0153] In the above explanation, plate heater 120 may also comprise a plate member comprising a heat conductor and a heat source arranged on the side of the plate member opposite to the heating side of the photothermographic (photosensitive) material.

[0154] When a photothermographic material does not contain a photosensitive silver halide, heat development is performed according to an ordinary method.

[0155] The present invention is described in detail with reference to the examples, but the present invention should not be construed as being limited thereto.

EXAMPLE 1-1

Preparation of Silver Halide Grain Emulsion 1

[0156] To 1,421 ml of distilled water were added 6.7 ml of a 1 wt% potassium bromide solution, 8.2 ml of 1 N nitric acid and 21.8 g of phthalated gelatin. This mixed solution was stirred in a titanium-coated stainless reaction vessel with maintaining the temperature at 25°C. Solution a1 (37.04 g of silver nitrate was diluted with distilled water to make 159 ml) and solution b1 (32.6 g of potassium bromide was diluted with distilled water to make 200 ml) were prepared. The entire amount of solution a1 was added to the reaction vessel at a constant flow rate by a controlled double jet method with maintaining pAg at 8.1 over 1 minute (solution b1 was added by a controlled double jet method). Then,

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30 ml of a 3.5 wt% hydrogen peroxide aqueous solution was added, further, 33.8 ml of a 3 wt% aqueous solution of benzimidazole was added thereto. Solution a2 (solution a1 was again diluted with distilled water to make 317.5 ml) and solution b2 (dipotassium hexachloroiridate was dissolved in solution b1 so as to make the concentration 1×10^{-4} mol per mol of the silver, diluted with distilled water to reach the final volume of 2 times of solution b1, i.e., 400 ml) were prepared. The entire amount of solution a2 was added to the reaction vessel at a constant flow rate by a controlled double jet method with maintaining pAg at 8.1 over 10 minutes (solution b2 was added by a controlled double jet method). Then, 50 ml of a 0.5 wt% methanol solution of 2-mercapto-5-methylbenzimidazole was added, further, pAg was lowered to 7.5 with silver nitrate, pH was adjusted with 1 N sulfuric acid to 3.8, and stirring was stopped. The reaction solution was subjected to precipitation, desalting and washing processes, 3.5 g of deionized gelatin was added, and then 1 N sodium hydroxide was added to adjust pH to 6.0 and pAg to 8.2, thereby a silver halide dispersion was obtained.

[0157] The grains in the thus-prepared silver halide emulsion were pure silver bromide grains having an average equivalent-sphere diameter of $0.031 \mu\text{m}$ and equivalent-sphere diameter variation coefficient of 11%. Grain size was the average of 1,000 grains obtained by electron microscope. {100} face ratio of this grain was 85% according to the Kubelka-Munk method.

[0158] The temperature of the above emulsion was raised to 45°C with stirring, then 5 ml of a 0.5 wt% methanol solution of N,N'-dihydroxy-N',N'-diethylmelamine and 5 ml of a 3.5 wt% methanol solution of phenoxyethanol were added thereto, and 1 minute after, 3×10^{-5} mol per mol of the silver of sodium benzenethiosulfonate was added. Further 2 minutes after, a solid dispersion of spectral sensitizing dye 1 (an aqueous gelatin solution) was added in an amount of 5×10^{-3} mol per mol of the silver, and further 2 minutes after, 5×10^{-5} mol per mol of the silver of a tellurium compound was added and the reaction solution was subjected to ripening for 50 minutes. Immediately before completion of ripening, 2-mercapto-5-methylbenzimidazole in an amount of 1×10^{-3} mol, and mercapto compound 1 in an amount of 1.1×10^{-3} mol, each per mol of the silver, were added to the reaction solution. The temperature was lowered to 32°C . Thus, silver halide grain emulsion 1 were prepared.

Preparation of Silver Halide Grain Emulsion 2

[0159] Phthalated gelatin (22 g) and 30 mg of potassium bromide were dissolved in 700 ml of water, pH was adjusted to 5.0 at 35°C . An aqueous solution (159 ml) containing 18.8 g of silver nitrate and 0.9 g of ammonium nitrate and an aqueous solution containing potassium bromide and potassium iodide in molar ratio of 92/8 were added to the foregoing solution by a controlled double jet method over 10 minutes with maintaining pAg at 7.7. Subsequently, 476 ml of an aqueous solution containing 55.4 g of silver nitrate and 2 g of ammonium nitrate and an aqueous solution containing 1×10^{-5} mol/liter of dipotassium hexachloroiridate and 1 mol/liter of potassium bromide were added to the foregoing solution by a controlled double jet method over 30 minutes with maintaining pAg at 7.7. Subsequently, 1 g of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added thereto, pH was lowered and the reaction solution was subjected to coagulative precipitation, and desalted. Then, 0.1 g of phenoxyethanol was added to adjust pH to 5.9 and pAg to 8.2, thereby the formation of silver iodobromide grains was terminated. The thus-obtained silver halide grains were cubic grains having an iodine content at core part: 8 mol%, average: 2 mol%, an average grain size of $0.005 \mu\text{m}$, a variation coefficient of the projected area diameter of 8%, and {100} face ratio of 88%.

[0160] The temperature of the thus-obtained silver halide grains was raised to 80°C . Sodium thiosulfate (85 μmol), 1.1×10^{-5} mol of 2,3,4,5,6-pentafluorophenylphenylphosphineselenide, 1.5×10^{-5} mol of a tellurium compound, 3.5×10^{-9} mol of chlorauric acid, and 2.7×10^{-4} mol of thiocyanic acid, each per mol of the silver, were added to the above silver halide grains and ripened for 120 minutes, then quenched to 40°C . Spectral sensitizing dye 1 in an amount of 1×10^{-4} mol and 2-mercapto-5-methylbenzimidazole in an amount of 5×10^{-4} mol were added thereto, and then the solution was quenched to 30°C , thereby silver halide grain emulsion 2 was obtained.

Preparation of Scaly Fatty Acid Silver Salt

[0161] Behenic acid (87.6 g) (manufactured by Henkel Co., trade name: Edenor C22-85R), 423 ml of distilled water, 49.2 ml of an aqueous solution containing 5 N NaOH, and 120 ml of tert-butanol were mixed, and the mixture was subjected to reaction for 1 hour at 75°C , thereby a sodium behenate solution was obtained. Apart from the sodium behenate solution, 206.2 ml of an aqueous solution containing 40.4 g of silver nitrate (pH 4.0) was prepared and maintained at 10°C . A reaction vessel containing 635 ml of distilled water and 30 ml of tert-butanol was maintained at 30°C , with stirring the content in the reaction vessel, the entire amount of the above sodium behenate solution and the entire amount of the aqueous silver nitrate solution were added to the reaction vessel at a constant flow rate over 62 minutes and 10 seconds and 60 minutes, respectively, in such a manner that only the aqueous silver nitrate solution was added from the start of the addition, 7 minutes and 20 seconds after the start of the addition of the aqueous silver nitrate solution, the addition of the sodium behenate solution was started, and only the sodium behenate solution was

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added for 9 minutes and 30 seconds after the termination of the addition of the aqueous silver nitrate solution. The temperature in the reaction vessel was maintained at 30°C and the outer temperature was controlled so as not to increase the temperature. The piping of the addition system of the sodium behenate solution was warmed by a steamed jacket method, and steam aperture was adjusted so that the solution temperature at the outlet of the addition nozzle tip became 75°C. The piping of the addition system of the aqueous silver nitrate solution was warmed by circulating chilled water in the outer pipe of the double pipe. The positions where the sodium behenate solution and the aqueous silver nitrate solution were added were arranged symmetrically with the stirring axle between, and the height of the position was adjusted so as not to touch the reaction solution.

[0162] After the addition of the sodium behenate solution was finished, the reaction solution was stirred at the same temperature for 20 minutes and allowed to stand to lower the temperature to 25°C. The solid content was then filtered by suction. The solid content was washed with water until the conductivity of the filtrate reached 30 µS/cm. Thus, a fatty acid silver salt was obtained. The solid content obtained was not dried and stored as a wet cake.

[0163] The shape of the obtained silver behenate particles was evaluated with an electron microscope. The obtained silver behenate particles were scaly crystals having $a = 0.14 \mu\text{m}$, $b = 0.4 \mu\text{m}$, and $c = 0.6 \mu\text{m}$, on average, and variation coefficient of the average equivalent-sphere diameter of 15%.

[0164] Polyvinyl alcohol (trade name: PVA-217) (7.4 g) and water were added to the wet cake of the amount corresponding to 100 g of dried solid content to make the entire amount 385 g, and then preliminarily dispersed in a homomixer.

[0165] The preliminarily dispersed starting solution was treated three times using a disperser (trade name: Microfluidizer M-110S-EH equipped with G10Z interaction chamber, manufactured by Micro Fluidex International Corp.). Pressure of the disperser was adjusted to 1,750 kg/cm². Thus, silver behenate dispersion was obtained. Cooling operation was performed by installing coiled heat exchangers respectively before and after the interaction chamber and setting the desired temperature of dispersion by adjusting the temperature of the cooling medium.

Preparation of Acicular Fatty Acid Silver Salt (comparison)

[0166] While stirring 43.8 g of behenic acid (manufactured by Henkel Co., trade name: Edenor C22-85R), 730 ml of distilled water, and 60 ml of tert-butanol at 79°C, 117 ml of an aqueous solution containing 1 N NaOH was added thereto over 55 minutes and the mixture was subjected to reaction for 240 minutes. Then, 112.5 ml of an aqueous solution containing 18.2 g of silver nitrate was added thereto over 45 seconds and the solution was allowed to stand for 20 minutes to lower the temperature to 30°C. The solid content was then filtered by suction. The solid content was washed with water until the conductivity of the filtrate reached 30 µS/cm. The thus-obtained solid content was not dried and treated as a wet cake. Polyvinyl alcohol (trade name: PVA-205) (7.4 g) and water were added to the wet cake of the amount corresponding to 100 g of dried solid content to make the entire amount 385 g, and then preliminarily dispersed in a homomixer.

[0167] The preliminarily dispersed starting solution was treated three times using a disperser (trade name: Microfluidizer M-110S-EH equipped with G10Z interaction chamber, manufactured by Micro Fluidex International Corp.). Pressure of the disperser was adjusted to 1,750 kg/cm². Thus, silver behenate dispersion B was obtained. Silver behenate particles contained in the thus-obtained silver behenate dispersion were acicular particles having $a = 0.04 \mu\text{m}$, $b = 0.04 \mu\text{m}$, and $c = 0.8 \mu\text{m}$, on average, and variation coefficient of 30%. Particle size was measured by Master Sizer X (manufactured by Malvern Instruments Ltd.). Cooling operation was performed by installing coiled heat exchangers respectively before and after the interaction chamber and setting the desired temperature of dispersion by adjusting the temperature of the cooling medium.

Preparation of 25 wt% Dispersion of Reducing Agent

[0168] Water (176 g) was added to 80 g of 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane and 64 g of a 20 wt% aqueous solution of modified polyvinyl alcohol Roval MP203 (manufactured by Kuraray Co., Ltd.), and thoroughly mixed to make a slurry. Zirconia beads (800 g) having an average diameter of 0.5 mm were added to a vessel with the above-obtained slurry and dispersed with a disperser (1/4 G sand grinder mill, manufactured by Imax Co., Ltd.) for 5 hours, thereby the dispersion of the reducing agent was obtained. The particles of the reducing agent contained in the thus-obtained reducing agent dispersion had an average particle diameter of 0.72 µm.

Preparation of 10 wt% Methanol Solution of Mercapto Compound

[0169] Ten (10) grams of 3-mercapto-4-phenyl-5-heptyl-1,2,4-triazole was dissolved in 90 g of methanol.

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Preparation of 20 wt% Dispersion of Mercapto Compound

[0170] Water (224 g) was added to 80 g of 3-mercapto-4-phenyl-5-heptyl-1,2,4-triazole and 32 g of a 20 wt% aqueous solution of modified polyvinyl alcohol Poval MP203 (manufactured by Kuraray Co., Ltd.), and thoroughly mixed to make a slurry. Zirconia beads (800 g) having an average diameter of 0.5 mm were added to a vessel with the above-obtained slurry and dispersed with a disperser (1/4 G sand grinder mill, manufactured by Imex Co., Ltd.) for 10 hours, thereby the dispersion of the mercapto compound was obtained. The particles of the mercapto compound contained in the thus-obtained mercapto compound dispersion had an average particle diameter of 0.67 μm .

Preparation of 30 wt% Dispersion of Organic Polyhalogen Compound

[0171] Water (224 g) was added to 44 g of tribromomethylphenylsulfone, 44 g of 3-tribromomethylsulfonyl-4-phenyl-5-tridecyl-1,2,4-triazole, 8 g of tribromomethyl-4-(2,4,6-trimethylphenylsulfonyl)phenylsulfone, 0.8 g of sodium trisopropyl- α -naphthalenesulfonate, and 48 g of a 20 wt% aqueous solution of modified polyvinyl alcohol Poval MP203 (manufactured by Kuraray Co., Ltd.), and thoroughly mixed to make a slurry. Zirconia beads (800 g) having an average diameter of 0.5 mm were added to a vessel with the above-obtained slurry and dispersed with a disperser (1/4 G sand grinder mill, manufactured by Imex Co., Ltd.) for 5 hours, thereby a dispersion of the organic polyhalogen compound was obtained. The particles of the organic polyhalogen compound contained in the thus-obtained polyhalogen compound dispersion had an average particle diameter of 0.74 μm .

Preparation of 10 wt% Methanol Solution of Phthalazine Compound

[0172] 8-Isopropylphthalazine (10 g) was dissolved in 90 g of methanol and used.

Preparation of 20 wt% Dispersion of Pigment

[0173] Water (250 g) was added to 64 g of C.I. Pigment Blue 60 and 6.4 g of Demol N (manufactured by Kao Corporation), and thoroughly mixed to make a slurry. Zirconia beads (800 g) having an average diameter of 0.5 mm were added to a vessel with the above-obtained slurry and dispersed with a disperser (1/4 G sand grinder mill, manufactured by Imex Co., Ltd.) for 25 hours, thereby the dispersion of the pigment was obtained. The particles of the pigment contained in the thus-obtained pigment dispersion had an average particle diameter of 0.21 μm .

Preparation of 40 wt% SBR Latex

[0174] SBR Latex purified by ultrafiltration was obtained as follows.

[0175] SBR latex shown below was diluted with distilled water to 10 times, and purified by module FS03-FC-FUY03A1 for ultrafiltration purification (Daisen Membrane System Co., Ltd.) until the ionic conductivity became 1.5 mS/cm. The concentration of the latex at this time was 40 wt%.

SBR Latex

[0176]

Latex of -St (68)-Bu (29)-AA (3)-

Equilibrium moisture content at 25°C 60% RH: 0.6 wt%

Average particle size: 0.1 μm

Concentration: 45 wt%

Ionic conductivity: 4.2 mS/cm

Ionic conductivity was measured using a conductometer CM-30S (manufactured by Toa Denpa Kogyo Co., Ltd.), and starting solution of the latex (40 wt%) was measured at 25°C.

pH: 8.2

Preparation of Coating Solution for Emulsion Layer (photosensitive layer)

[0177] The above-obtained 20 wt% dispersion of pigment (1.1 g), 103 g of organic acid silver dispersion, 5 g of the 20 wt% aqueous solution of modified polyvinyl alcohol MP-203 (manufactured by Kuraray Co., Ltd.), 25 g of the above-prepared 25 wt% reducing agent dispersion, 11.5 g of the 30 wt% dispersion of organic polyhalogen compound, 3.1 g of the 20 wt% dispersion of mercapto compound, 108 g of the 40 wt% SBR latex purified by ultrafiltration, and 8 ml of

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the 10 wt% solution of phthalazine compound were mixed, thereby an organic acid silver-containing solution was obtained. Silver halide grain emulsion 1 (5 g) and silver halide emulsion 2 (5 g) had been thoroughly mixed, stirred for 20 minutes, 10 ml of distilled water had been added thereto, and mixed with the foregoing organic acid silver-containing solution immediately before coating, by a static mixer to thereby prepare an emulsion layer coating solution. This coating solution was fed to a coating die as it was in a coating silver amount of 1.4 g/m².

[0178] The above emulsion layer coating solution was revealed to have viscosity of 85 (mPa·s) at 40°C (No. 1 rotor) measured by Model B viscometer (manufactured by Tokyo Kelki Co., Ltd.).

[0179] The viscosity of the coating solution measured by RFS Fluid Spectrometer (manufactured by Rheometrics Far East Co.) at 25°C was 1,500, 220, 70, 40, 20 (mPa·s) at shear rate of 0.1, 1, 10, 100, 1,000 (1/sec), respectively.

Preparation of Interlayer Coating Solution of Emulsion Surface

[0180] To 772 g of polyvinyl alcohol PVA-205 (manufactured by Kuraray Co., Ltd.), an alkali solution (a 20 wt% solution of NH₄OH as NH₄⁺, a 20 wt% solution of LiOH as Li⁺, and a 20 wt% solution of NaOH as Na⁺ were used respectively) in an addition amount shown in Tables I-1 to I-5, 0.5 g of the 20 wt% dispersion of pigment, and 226 g of a 27.5 wt% solution of latex of methyl methacrylate/styrene/2-ethylhexyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization weight ratio: 59/9/28/5/1) was added 2 ml of a 5 wt% aqueous solution of Aerosol OT (manufactured by American Cyanamide Co.) to make an interlayer coating solution, which was coated in a coating amount of 10 ml/m².

[0181] The viscosity of the coating solution was 21 (mPa·s) at 40°C (No. 1 rotor) measured by Model B viscometer.

Preparation of First Protective Layer Coating Solution of Emulsion Surface

[0182] Inert gelatin (80 g) was dissolved in water, and 0.3 g of the 20 wt% dispersion of pigment, a 10 wt% methanol solution of phthalic acid, 74 ml of a 10 wt% aqueous solution of 4-methylphthalic acid, 28 ml of 1 N sulfuric acid, and 5 ml of a 5 wt% aqueous solution of Aerosol OT (manufactured by American Cyanamide Co.) were added thereto. Water was added to make the total amount 1,000 g, thereby a first protective layer coating solution of emulsion surface was obtained, which was coated in a coating amount of 30 ml/m².

[0183] The viscosity of the coating solution was 17 (mPa·s) at 40°C (No. 1 rotor) measured by Model B viscometer.

A coating solution in which polyvinyl alcohol was used in place of gelatin was prepared.

Preparation of Second Protective Layer Coating Solution of Emulsion Surface

[0184] Inert gelatin (100 g) was dissolved in water, and 0.2 g of the 20 wt% dispersion of pigment, 20 ml of a 5 wt% solution of potassium N-perfluorooctylsulfonyl-N-propylalanine, 16 ml of a 5 wt% solution of Aerosol OT (manufactured by American Cyanamide Co.), 25 g of polymethyl methacrylate fine particles (average particle size: 4.0 μm), 1.4 g of phthalic acid, 1.6 g of 4-methylphthalic acid, 44 ml of 1 N sulfuric acid, and 445 ml of a 4 wt% chrome alum were added thereto. Water was added to make the total amount 2,000 g, thereby a second protective layer coating solution was obtained, which was coated in coating amount of 20 ml/m².

[0185] The viscosity of the coating solution was 9 (mPa·s) at 40°C (No. 1 rotor) measured by Model B viscometer. A coating solution in which polyvinyl alcohol was used in place of gelatin and boric acid was used in place of chrome alum was prepared.

Preparation of PET Support

[0186] PET having an intrinsic viscosity IV = 0.66 (measured in phenol/tetrachloroethane (8/4 by weight) at 25°C) was obtained according to ordinary method using terephthalic acid and ethylene glycol. After the obtained PET was pelletized and dried at 130°C for 4 hours, melted at 300°C, extruded from T-die, and suddenly cooled, thereby an unstretched film having a film thickness after thermal fixation of 175 μm was obtained.

[0187] The film was stretched to 3.3 times in the machine direction with rollers having different peripheral speeds, then 4.5 times in the transverse direction by means of a tenter. The temperatures at that time were 110°C and 130°C respectively. Subsequently, the film was subjected to thermal fixation at 240°C for 20 seconds, then relaxation by 4% in the transverse direction at the same temperature. The chuck part of the tenter was then slit, and both edges of the film were knurled. The film was rolled at 4 kg/cm², thereby a roll of film having a thickness of 175 μm was obtained.

Corona Discharge Treatment of Support Surface

[0188] Both surfaces of the support were put under room temperature and corona discharge treatment was performed

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at 20 m/min with a solid state corona treating apparatus model 6KVA manufactured by Piller Co. From the reading of electric current/voltage, treatment applied to the support at that time was revealed to be 0.375 kV·A·min/m². The frequency at treatment at that time was 9.6 kHz and the gap clearance between the electrode and the dielectric roll was 1.8 mm.

Preparation of Undercoated Support

(1) Undercoating

(1-1) Undercoating Tayer Coating

[0189]

Prescription (1) (first layer)

Butadiene/styrene copolymer latex (solid content: 43 wt%, weight ratio of butadiene/styrene: 32/68)	13 ml
8 wt% aqueous solution of sodium 2,4-dichloro-6-hydroxy-s-triazine	7 ml
1 wt% aqueous solution of sodium lauryl-benzenesulfonate	1.8 ml
Distilled water	80 ml

Prescription (2) (second layer on the photosensitive layer side)

Gelatin	0.9 g
20 wt% dispersion of pigment	1 g
Methyl cellulose (Metolose SM15, substitution degree: 1.79 to 1.83)	0.1 g
Acetic acid (concentration: 99 wt%)	0.02 ml
Distilled water	98 ml

Prescription (3) (second layer on the back surface side)

SnO ₂ /Sb (9/1 by weight, average particle size: 0.25 μm)	100 mg/m ²
Gelatin	77 mg/m ²
Sodium dodecylbenzenesulfonate	1 mg/m ²
Sodium dihexyl-α-sulfosuccinate	4 mg/m ²

Preparation of Undercoated Support

[0190] Both surfaces of the above-prepared biaxially stretched polyethylene terephthalate support having a film thickness of 175 μm were subjected to corona discharge treatment, then the above undercoating solution prescription (1) was coated by means of a wire bar in a wet coating amount of 8 ml/m² (per one surface side) and dried at 180°C for 5 minutes. Subsequently, one surface (photosensitive layer side) was subjected to corona discharge treatment, then the above undercoating solution prescription (2) was coated by means of a wire bar in a wet coating amount of 9 ml/m² and dried at 180°C for 5 minutes. The back surface was coated with undercoating solution prescription (3) by means of a wire bar in a wet coating amount of 5 ml/m² and dried at 180°C for 5 minutes. Thus, the undercoated support was prepared.

Preparation of Back Coating Solution

Preparation of Solid Fine Particle Dispersion Solution (a) of Base Precursor

[0191] A base precursor compound 11 shown below (84 g), 28 g of a diphenylsulfone compound 12 shown below, and 10 g of surfactant Demole N (manufactured by Kao Corporation) were mixed with 220 ml of distilled water. The mixed solution was dispersed using beads in a sand mill (1/4 Gallon sand grinder mill, manufactured by Imex Co., Ltd.), thereby a solid fine particle co-dispersion solution (a) of the base precursor compound and the diphenylsulfone compound having an average particle size of 0.2 μm was obtained.

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Preparation of Solid Fine Particle Dispersion Solution of Dye

[0192] Cyanine dye compound 13 shown below (9.6 g) and 5.8 g of sodium p-alkylbenzenesulfonate were mixed with 305 ml of distilled water. The mixed solution was dispersed using beads in a sand mill (1/4 Gallon sand grinder mill, manufactured by Imex Co., Ltd.), thereby a solid fine particle dispersion solution of the dye having an average particle size of 0.2 μm was obtained.

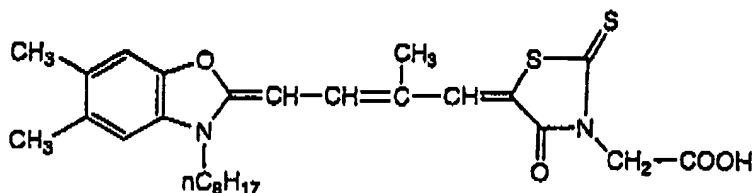
Preparation of Antihalation Layer Coating Solution

[0193] PVA-217 (17 g), 9.6 g of polyacrylamide, 70 g of the above solid fine particle dispersion solution (a) of the base precursor, 56 g of the above solid fine particle dispersion solution of the dye, 1.5 g of polymethyl methacrylate fine particles (average particle size: 6.5 μm), 2.2 g of sodium polyethylenesulfonate, 0.2 g of a coloring dye compound 14, and 844 ml of H_2O were mixed. Thus, an antihalation layer coating solution was prepared.

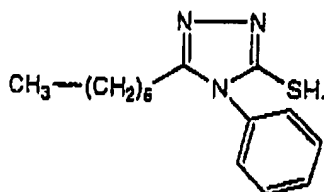
Preparation of Back Surface Protective Layer Coating Solution

[0194] To a reaction vessel maintained at 40°C were added and mixed 50 g of PVA-117, 0.2 g of sodium polystyrenesulfonate, 2.4 g of N,N'-ethylenebis(vinyl sulfone acetamide), 1 g of sodium t-octylphenoxyethoxyethanesulfonate, 30 mg of compound 15, 32 mg of $C_8F_{17}SO_3K$, 64 mg of $C_8F_{17}SO_3N(C_6H_{17})(CH_2CH_2O)_4(CH_2)_4-SO_3Na$, 8.8 g of acrylic acid/ethyl acrylate copolymer (copolymerization weight ratio: 5/95), and 950 ml of H_2O to prepare a back surface protective layer coating solution.

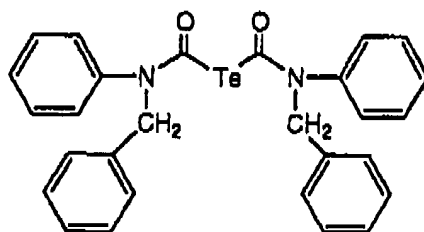
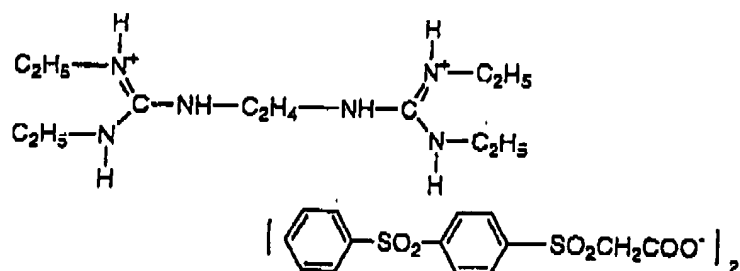
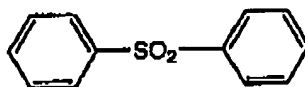
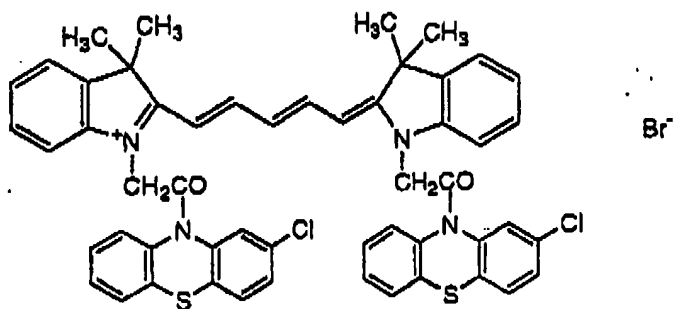
Spectral Sensitizing Dye 1



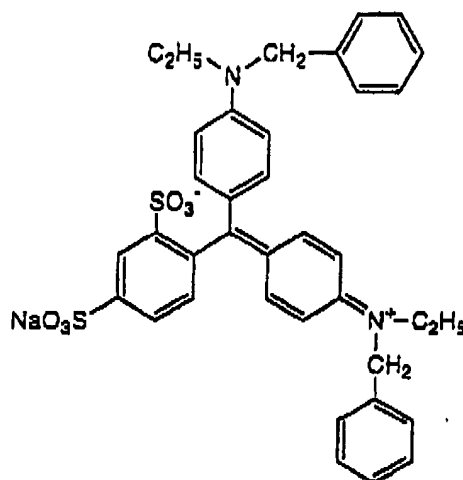
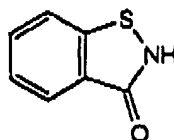
Mercuric Compound 1



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Tellurium CompoundBase Precursor Compound 11Compound 12Cyanine Dye Compound 13

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Blue Dye Compound 14Compound 15Preparation of Photothermographic Photosensitive Material

[0195] On the back side surface of the above-undercoated polyethylene terephthalate support, antihalation layer coating solution and the back surface protective layer coating solution were simultaneously coated and dried in such a manner that the coating amount of the solid content of the solid fine particle dye of antihalation layer coating solution became 0.04 g/m² and the PVA coating amount of the back surface protective layer coating solution became 1 g/m², thereby an antihalation backing layer was prepared.

[0196] The emulsion layer, the interlayer, the first protective layer and the second protective layer were simultaneously multilayer-coated by slide bead coating method on the opposite side of the backing layer side in this order from the undercoating side, thereby photothermographic (photosensitive) material Sample was prepared.

[0197] Coating speed was 160 m/min. The distance between the tip of the coating die and the support was 0.18 mm. The pressure in the low pressure chamber was set lower than atmospheric pressure by 392 Pa. In the subsequent chilling zone, air of dry-bulb temperature of 18°C and wet-bulb temperature of 12°C was blown for 30 seconds. After the coating solution was dried, dry air of dry-bulb temperature of 30°C and wet-bulb temperature of 18°C was blown at helical floating type drying zone for 200 seconds. The sample was then passed through drying zone at 70°C for 30 seconds, and then cooled to 25°C, thereby the solvent in the coating solution was evaporated. In the chilling zone and drying zone, the average wind speed was 7 m/sec.

Evaluation of Silver Tone Due to Variation of Heat Development Condition

[0198] The sample of photothermographic (photosensitive) material prepared was subjected to stepwise gradation exposure with laser beams vertically multiplied by applying high frequency convolution using a semiconductor laser emitting at 660 nm. Then, heat development was performed for 20 seconds at temperatures of 117°C, 120°C and 123°C with heat developing device 10 of a plate heater type described in Fig. 1 in JP-A-11-133572, and the difference

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of silver tone due to variation of heat development condition was evaluated visually according to the following criteria. The sample was deodorized with metal mesh and an active carbon filter.

L: Difference of silver tone due to temperature condition is large and impracticable.

M: Difference of silver tone due to temperature condition is observed but in allowable range.

S: Difference of silver tone due to temperature condition is not observed and good.

[0199] The silver tone obtained by heat development at 120°C for 20 seconds was visually evaluated.

⊙: Pure blackish silver tone, favorable.

○: Deviated a little from pure black but is good.

Δ: A trace of a tincture of magenta, or a tincture of cyan, or a tincture of yellow is observed, allowable.

Δ^x: A tincture of magenta, or a tincture of cyan, or a tincture of yellow is considerably observed, but is allowable.

x: A tincture of magenta, or a tincture of cyan, or a tincture of yellow is strong, impracticable.

Evaluation of Storage Stability

[0200] Difference in Dmin between the sample of the prepared photothermographic (photosensitive) material which was allowed to stand at 35°C 70% RH for 7 days as a coated bulk product and a sample which was refrigerated for 7 days as a coated bulk product was measured. Each sample was subjected to stepwise gradation exposure with a semiconductor laser emitting at 680 nm not applying high frequency convolution. Then, heat development was performed for 20 seconds at 120°C with the same heat developing device 10. Difference in Dmin was expressed as the difference in measured V value of Macbeth densitometer.

[0201] The results obtained are shown in Tables I-1 to I-5. In Tables I-1, I-4 and I-5, samples in which gelatin is used as the main binder in the first and second layers are shown, and in Tables I-2 and I-3, samples in which PVA is used as the main binder in the first and second layers are shown.

TABLE I-1

Series using gelatin in the first and second protective layers				
Sample No.	Shape of Organic Acid Silver	Alkali Ion (mmol/m ²)	Storage Stability of Coated Bulk Product	Silver Tone Difference
1 (Comparison)	Acicular	-	0.47	L
2 (Comparison)	Acicular	NH ₄ ⁺ (0.28)	0.41	L
3 (Comparison)	Acicular	NH ₄ ⁺ (1.11)	0.38	L
4 (Comparison)	Acicular	NH ₄ ⁺ (2.11)	0.42	L
5 (Comparison)	Acicular	NH ₄ ⁺ (3.89)	0.51	L
6 (Comparison)	Scaly	-	0.14	L
7 (Invention)	Scaly	NH ₄ ⁺ (0.28)	0.08	M
8 (Invention)	Scaly	NH ₄ ⁺ (1.11)	0.07	S
9 (Invention)	Scaly	NH ₄ ⁺ (2.11)	0.08	S
10 (Comparison)	Scaly	NH ₄ ⁺ (3.89)	0.18	S

TABLE I-2

Series using PVA in the first and second protective layers				
Sample No.	Shape of Organic Acid Silver	Alkali Ion (mmol/m ²)	Storage Stability of Coated Bulk Product	Silver Tone Difference
11 (Comparison)	Acicular	-	0.46	L
12 (Comparison)	Acicular	NH ₄ ⁺ (0.28)	0.39	L
13 (Comparison)	Acicular	NH ₄ ⁺ (1.11)	0.38	L

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TABLE I-2 (continued)

Series using PVA in the first and second protective layers				
Sample No.	Shape of Organic Acid Silver	Alkali Ion (mmol/m ²)	Storage Stability of Coated Bulk Product	Silver Tone Difference
14 (Comparison)	Acicular	NH ₄ ⁺ (2.11)	0.41	L
15 (Comparison)	Acicular	NH ₄ ⁺ (3.89)	0.50	L
16 (Comparison)	Scaly	-	0.13	L
17 (Invention)	Scaly	NH ₄ ⁺ (0.28)	0.08	M
18 (Invention)	Scaly	NH ₄ ⁺ (1.11)	0.07	S
19 (Invention)	Scaly	NH ₄ ⁺ (2.11)	0.07	S
20 (Comparison)	Scaly	NH ₄ ⁺ (3.89)	0.17	S

TABLE I-3

Series using PVA in the first and second protective layers				
Sample No.	Shape of Organic Acid Silver	Alkali Ion (mmol/m ²)	Storage Stability of Coated Bulk Product	Silver Tone Difference
31 (Comparison)	Acicular	-	0.47	L
32 (Comparison)	Acicular	Li ⁺ (0.14)	0.42	L
33 (Comparison)	Acicular	Li ⁺ (0.72)	0.39	L
34 (Comparison)	Acicular	Li ⁺ (2.18)	0.44	L
35 (Comparison)	Acicular	Li ⁺ (4.32)	0.54	L
36 (Comparison)	Scaly	-	0.14	L
37 (Invention)	Scaly	Li ⁺ (0.14)	0.10	M
38 (Invention)	Scaly	Li ⁺ (0.72)	0.09	S
39 (Invention)	Scaly	Li ⁺ (2.18)	0.08	S
40 (Comparison)	Scaly	Li ⁺ (4.32)	0.20	S

TABLE I-4

Series using gelatin in the first and second protective layers				
Sample No.	Shape of Organic Acid Silver	Alkali Ion (mmol/m ²)	Storage Stability of Coated Bulk Product	Silver Tone Difference
41 (Comparison)	Acicular	-	0.47	L
42 (Comparison)	Acicular	Na ⁺ (0.12)	0.45	L
43 (Comparison)	Acicular	Na ⁺ (0.82)	0.32	L
44 (Comparison)	Acicular	Na ⁺ (1.64)	0.42	L
45 (Comparison)	Acicular	Na ⁺ (5.22)	0.52	L
46 (Comparison)	Scaly	-	0.14	L
47 (Invention)	Scaly	Na ⁺ (0.12)	0.08	M
48 (Invention)	Scaly	Na ⁺ (0.82)	0.05	S
49 (Invention)	Scaly	Na ⁺ (1.64)	0.09	S
50 (Comparison)	Scaly	Na ⁺ (5.22)	0.18	S

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TABLE 1-5
Series using gelatin in the first and second protective layers

Sample No.	Shape of Organic Acid Silver	NH ₄ ⁺ Amount (mmol/m ²)	Na ⁺ Amount (mmol/m ²)	NH ₄ ⁺ /Na ⁺ Mol Ratio	Storage Stability of Coated Bulk Product	Silver Tone Difference	Silver Tone
1 (Comparison)	Acicular	1.58	—	∞	0.42	L	A*
2 (Comparison)	Acicular	1.58	0.03	52.6	0.38	L	A
3 (Comparison)	Acicular	1.58	0.12	13.2	0.45	L	O
4 (Comparison)	Acicular	1.58	0.82	1.9	0.40	L	●
5 (Comparison)	Acicular	0.79	0.82	0.96	0.37	L	●
6 (Comparison)	Acicular	0.12	0.82	0.14	0.52	L	O
7 (Comparison)	Acicular	0.03	0.82	0.04	0.61	L	A
8 (Comparison)	Acicular	—	0.82	0	0.55	L	A*
9 (Invention)	Scaly	1.58	0	∞	0.07	S	A*
10 (Invention)	Scaly	1.58	0.03	52.6	0.08	S	A
11 (Invention)	Scaly	1.58	0.12	13.2	0.05	S	O
12 (Invention)	Scaly	1.58	0.82	1.9	0.04	S	●
13 (Invention)	Scaly	0.79	0.82	0.96	0.03	S	●
14 (Invention)	Scaly	0.12	0.82	0.14	0.07	S	O
15 (Invention)	Scaly	0.03	0.82	0.04	0.06	S	A
16 (Invention)	Scaly	0	0.82	0	0.07	S	A*

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[0202] From the results in Tables I-1, I-2, I-3, I-4 and I-5, the effect of the present invention is apparent. Samples according to the present invention are excellent in photographic properties.

EXAMPLE I-2

[0203] Samples were prepared in the same manner as in Example I-1 except that SBR latex used in emulsion layers was not purified. The same results as in Example I-1 were obtained.

EXAMPLE I-3

[0204] Samples were prepared in the same manner as in Example I-1 except that latexes Lb1 and Lc1 (equilibrium moisture content at 25°C 60% RH was less than 2 wt% with both Lb1 and Lc1) shown below were used in place of SBR latex used in emulsion layers.

[0205] The same results as in Example I-1 were obtained.

Synthesis of Lb1

[0206] Into a glass autoclave (TEM-V1000, manufactured by Taiatsu Glass Kogyo Co., Ltd.) were put 140 g of styrene, 280 g of distilled water, 4.44 g of a surfactant (Sandet BL, manufactured by Sanyo Kasei Co., Ltd.), and 6 g of acrylic acid, and the content was stirred for 1 hour in a nitrogen atmosphere. Thereafter, 54 g of 2-ethylhexyl acrylate was added to the reaction mixture and the temperature was raised to 70°C. Then, 20 g of a 5 wt% aqueous ammonium persulfate solution was added thereto and stirring was continued for 10 hours. After stirring was finished, the temperature of the reaction vessel was lowered to room temperature, thereby a styrene-acryl latex was obtained. 1 N aqueous ammonia was added to this latex to adjust pH to 7.5.

[0207] Thus, latex Lb1 having an average particle diameter of 98 nm and concentration of 42 wt% was obtained. Equilibrium moisture content of the polymer at 25°C 60% RH was 0.7 wt%.

Synthesis of Lc1

[0208] Into a glass autoclave (TEM-V1000, manufactured by Taiatsu Glass Kogyo Co., Ltd.) were put 126 g of methyl methacrylate, 280 g of distilled water, 8.2 g of a surfactant (Sandet BL, manufactured by Sanyo Kasei Co., Ltd.), and 4 g of acrylic acid, and the content was stirred for 1 hour in a nitrogen atmosphere. Thereafter, 70 g of ethyl acrylate was added to the reaction mixture and the temperature was raised to 80°C. Then, 20 g of a 5 wt% aqueous potassium persulfate solution was added thereto and stirring was continued for 10 hours. After stirring was finished, the temperature of the reaction vessel was lowered to room temperature, thereby an acryl latex was obtained. 1 N aqueous ammonia was added to this latex to adjust pH to 7.5.

[0209] Thus, latex Lc1 having an average particle diameter of 101 nm and concentration of 44 wt% was obtained. Equilibrium moisture content of the polymer at 25°C 60% RH was 0.7 wt%.

EXAMPLE I-4

[0210] Samples were prepared in the same manner as in Examples I-1 to I-3 except that photosensitive silver halide was excluded. The obtained samples were heated to 100°C or more with a thermosensitive type thermal head (maximum temperature: 230°C). The same results as in Examples I-1 to I-3 were obtained.

EXAMPLE II-1Preparation of Silver Halide Grains 1

[0211] To 1,421 ml of distilled water were added 6.7 ml of a 1 wt% potassium bromide solution, 8.2 ml of 1 N nitric acid and 21.8 g of phthalated gelatin. This mixed solution was stirred in a titanium-coated stainless reaction vessel with maintaining the temperature at 25°C. Solution a1 (37.04 g of silver nitrate was diluted with distilled water to make 159 ml) and solution b1 (32.6 g of potassium bromide was diluted with distilled water to make 200 ml) were prepared. The entire amount of solution a1 was added to the reaction vessel at a constant flow rate by a controlled double jet method with maintaining pAg at 8.1 over 1 minute (solution b1 was added by a controlled double jet method). Then, 30 ml of a 3.5 wt% hydrogen peroxide aqueous solution was added, further, 33.6 ml of a 3 wt% aqueous solution of benzimidazole was added thereto. Solution a2 (solution a1 was again diluted with distilled water to make 317.5 ml) and solution b2 (dipotassium hexachloroiridate was dissolved in solution b1 so as to make the concentration 1×10^{-4}

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mol per mol of the silver, diluted with distilled water to reach the final volume of 2 times of solution b1, i.e., 400 ml) were prepared. The entire amount of solution a2 was added to the reaction vessel at a constant flow rate by a controlled double jet method with maintaining pAg at 8.1 over 10 minutes (solution b2 was added by a controlled double jet method). Then, 50 ml of a 0.5 wt% methanol solution of 2-mercapto-5-methylbenzimidazole was added, further, pAg was lowered to 7.5 with silver nitrate, pH was adjusted with 1 N sulfuric acid to 3.8, and stirring was stopped. The reaction solution was subjected to precipitation, desalting and washing processes, 3.5 g of deionized gelatin was added, and then 1 N sodium hydroxide was added to adjust pH to 6.0 and pAg to 8.2, thereby a silver halide dispersion was obtained.

[0212] The grains in the thus-prepared silver halide emulsion were pure silver bromide grains having an average equivalent-sphere diameter of 0.031 μm and equivalent-sphere diameter variation coefficient of 11%. Grain size was the average of 1,000 grains obtained by electron microscope. {100} face ratio of this grain was 85% according to the Kubelka-Munk method.

[0213] The temperature of the above emulsion was raised to 45°C with stirring, then 5 ml of a 0.5 wt% methanol solution of N,N'-dihydroxy-N,N'-diethylmelamine and 5 ml of a 3.5 wt% methanol solution of phenoxyethanol were added thereto, and 1 minute after, 3×10^{-5} mol per mol of the silver of sodium benzenethiosulfonate was added. Further 2 minutes after, a solid dispersion of spectral sensitizing dye 1 (an aqueous gelatin solution) was added in an amount of 5×10^{-3} mol per mol of the silver, and further 2 minutes after, 5×10^{-5} mol per mol of the silver of a tellurium compound was added and the reaction solution was subjected to ripening for 50 minutes. Immediately before completion of ripening, 2-mercapto-5-methylbenzimidazole in an amount of 1×10^{-3} mol, and mercapto compound 1 in an amount of 1.1×10^{-3} mol, each per mol of the silver, were added to the reaction solution. The temperature was lowered to 32°C. Thus, silver halide grains 1 were prepared.

Preparation of Silver Halide Grains 2

[0214] Phthalated gelatin (22 g) and 30 mg of potassium bromide were dissolved in 700 ml of water, pH was adjusted to 5.0 at 35°C. An aqueous solution (159 ml) containing 18.8 g of silver nitrate and 0.9 g of ammonium nitrate and an aqueous solution containing potassium bromide and potassium iodide in molar ratio of 92/8 were added to the foregoing solution by a controlled double jet method over 10 minutes with maintaining pAg at 7.7. Subsequently, 478 ml of an aqueous solution containing 55.4 g of silver nitrate and 2 g of ammonium nitrate and an aqueous solution containing 1×10^{-5} mol/liter of dipotassium hexachloroiridate and 1 mol/liter of potassium bromide were added to the foregoing solution by a controlled double jet method over 30 minutes with maintaining pAg at 7.7. Subsequently, 1 g of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added thereto, pH was lowered and the reaction solution was subjected to coagulation precipitation, and desalted. Then, 0.1 g of phenoxyethanol was added to adjust pH to 5.9 and pAg to 8.2, thereby the formation of silver iodobromide grains was terminated. The thus-obtained silver halide grains were cubic grains having an iodine content at core part: 8 mol%, average: 2 mol%, an average grain size of 0.005 μm , a variation coefficient of the projected area diameter of 8%, and {100} face ratio of 88%.

[0215] The temperature of the thus-obtained silver halide grains was raised to 60°C. Sodium thiosulfate (85 μmol), 1.1×10^{-5} mol of 2,3,4,5,6-pentafluorophenyldiphenylphosphineoxide, 1.5×10^{-5} mol of a tellurium compound, 3.5×10^{-5} mol of chlorosulfuric acid, and 2.7×10^{-4} mol of thiocyanic acid, each per mol of the silver, were added to the above silver halide grains and ripened for 120 minutes, then quenched to 40°C. Spectral sensitizing dye 1 in an amount of 1×10^{-4} mol and 2-mercapto-5-methylbenzimidazole in an amount of 5×10^{-4} mol were added thereto, and then the solution was quenched to 30°C, thereby silver halide emulsion 2 was obtained.

Preparation of Scalp Fatty Acid Silver Salt

[0216] Behenic acid (87.6 g) (manufactured by Henkel Co., trade name: Edenor C22-85R), 423 ml of distilled water, 49.2 ml of an aqueous solution containing 5 N NaOH, and 120 ml of tert-butanol were mixed, and the mixture was subjected to reaction for 1 hour at 75°C, thereby a sodium behenate solution was obtained. Apart from the sodium behenate solution, 208.2 ml of an aqueous solution containing 40.4 g of silver nitrate (pH 4.0) was prepared and maintained at 10°C. A reaction vessel containing 635 ml of distilled water and 30 ml of tert-butanol was maintained at 30°C, with stirring the content in the reaction vessel, the entire amount of the above sodium behenate solution and the entire amount of the aqueous silver nitrate solution were added to the reaction vessel at a constant flow rate over 62 minutes and 10 seconds and 60 minutes, respectively, in such a manner that only the aqueous silver nitrate solution was added from the start of the addition, 7 minutes and 20 seconds after the start of the addition of the aqueous silver nitrate solution, the addition of the sodium behenate solution was started, and only the sodium behenate solution was added for 9 minutes and 30 seconds after the termination of the addition of the aqueous silver nitrate solution. The temperature in the reaction vessel was maintained at 30°C and the outer temperature was controlled so as not to increase the temperature. The piping of the addition system of the sodium behenate solution was warmed by a steamed

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jacket method, and steam aperture was adjusted so that the solution temperature at the outlet of the addition nozzle tip became 75°C. The piping of the addition system of the aqueous silver nitrate solution was warmed by circulating chilled water in the outer pipe of the double pipe. The positions where the sodium behenate solution and the aqueous silver nitrate solution were added were arranged symmetrically with the stirring axle between, and the height of the position was adjusted so as not to touch the reaction solution.

[0217] After the addition of the sodium behenate solution was finished, the reaction solution was stirred at the same temperature for 20 minutes and allowed to stand to lower the temperature to 25°C. The solid content was then filtered by suction. The solid content was washed with water until the conductivity of the filtrate reached 30 $\mu\text{S}/\text{cm}$. Thus, a fatty acid silver salt was obtained. The solid content obtained was not dried and stored as a wet cake.

[0218] The shape of the obtained silver behenate particles was evaluated with an electron microscope. The obtained silver behenate particles were scaly crystals having $a = 0.14 \mu\text{m}$, $b = 0.4 \mu\text{m}$, and $c = 0.8 \mu\text{m}$, on average, and variation coefficient of the average equivalent-sphere diameter of 15%.

[0219] Polyvinyl alcohol (trade name: PVA-217) (7.4 g) and water were added to the wet cake of the amount corresponding to 100 g of dried solid content to make the entire amount 385 g, and then preliminarily dispersed in a homomixer.

[0220] The preliminarily dispersed starting solution was treated three times using a disperser (trade name: Microfluidizer M-110S-EH equipped with G10Z interaction chamber, manufactured by Micro Fluidex International Corp.). Pressure of the disperser was adjusted to 1,750 kg/cm^2 . Thus, silver behenate dispersion was obtained. Cooling operation was performed by installing cooled heat exchangers respectively before and after the interaction chamber and setting the desired temperature of dispersion by adjusting the temperature of the cooling medium.

Preparation of Acicular Fatty Acid Silver Salt (comparison)

[0221] While stirring 43.8 g of behenic acid (manufactured by Henkel Co., trade name: Edenor C22-85R), 730 ml of distilled water, and 60 ml of tert-butanol at 79°C, 117 ml of an aqueous solution containing 1 N NaOH was added thereto over 55 minutes and the mixture was allowed to reaction for 240 minutes. Then, 112.5 ml of an aqueous solution containing 19.2 g of silver nitrate was added thereto over 45 seconds and the solution was allowed to stand for 20 minutes to lower the temperature to 30°C. The solid content was then filtered by suction. The solid content was washed with water until the conductivity of the filtrate reached 30 $\mu\text{S}/\text{cm}$. The thus-obtained solid content was not dried and treated as a wet cake. Polyvinyl alcohol (trade name: PVA-205) (7.4 g) and water were added to the wet cake of the amount corresponding to 100 g of dried solid content to make the entire amount 385 g, and then preliminarily dispersed in a homomixer.

[0222] The preliminarily dispersed starting solution was treated three times using a disperser (trade name: Microfluidizer M-110S-EH equipped with G10Z interaction chamber, manufactured by Micro Fluidex International Corp.). Pressure of the disperser was adjusted to 1,750 kg/cm^2 . Thus, silver behenate dispersion B was obtained. Silver behenate particles contained in the thus-obtained silver behenate dispersion were acicular particles having $a = 0.04 \mu\text{m}$, $b = 0.04 \mu\text{m}$, and $c = 0.8 \mu\text{m}$, on average, and variation coefficient of 30%. Particle size was measured by Master Sizer X (manufactured by Malvern Instruments Ltd.). Cooling operation was performed by installing cooled heat exchangers respectively before and after the interaction chamber and setting the desired temperature of dispersion by adjusting the temperature of the cooling medium.

Preparation of 25 wt% Dispersion of Reducing Agent

[0223] Water (178 g) was added to 80 g of 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane and 64 g of a 20 wt% aqueous solution of modified polyvinyl alcohol Poval MP203 (manufactured by Kuraray Co., Ltd.), and thoroughly mixed to make a slurry. Zirconia beads (800 g) having an average diameter of 0.5 mm were added to a vessel with the above-obtained slurry and dispersed with a disperser (1/4 G sand grinder mill, manufactured by Imex Co., Ltd.) for 5 hours, thereby the dispersion of the reducing agent was obtained. The particles of the reducing agent contained in the thus-obtained reducing agent dispersion had an average particle diameter of 0.72 μm .

Preparation of 10 wt% Methanol Solution of Mercapto Compound

[0224] Ten (10) grams of 3-mercapto-4-phenyl-5-heptyl-1,2,4-triazole was dissolved in 90 g of methanol.

Preparation of 20 wt% Dispersion of Mercapto Compound

[0225] Water (224 g) was added to 64 g of 3-mercapto-4-phenyl-5-heptyl-1,2,4-triazole and 32 g of a 20 wt% aqueous solution of modified polyvinyl alcohol Poval MP203 (manufactured by Kuraray Co., Ltd.), and thoroughly mixed to make

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a slurry. Zirconia beads (800 g) having an average diameter of 0.5 mm were added to a vessel with the above-obtained slurry and dispersed with a disperser (1/4 G sand grinder mill, manufactured by Imex Co., Ltd.) for 10 hours, thereby the dispersion of the mercapto compound was obtained. The particles of the mercapto compound contained in the thus-obtained mercapto compound dispersion had an average particle diameter of 0.67 μm .

Preparation of 30 wt% Dispersion of Organic Polyhalogen Compound

[0226] Water (224 g) was added to 44 g of tribromomethylphenylsulfone, 44 g tribromomethylsulfonyl-4-phenyl-5-tridecyl-1,2,4-triazole, 8 g of tribromomethyl-4-(2,4,6-trimethylphenylsulfonyl)phenylsulfone, 0.8 g of sodium triisopropyl- α -naphthalenesulfonate, and 48 g of a 20 wt% aqueous solution of modified polyvinyl alcohol Poval MP203 (manufactured by Kuraray Co., Ltd.), and thoroughly mixed to make a slurry. Zirconia beads (800 g) having an average diameter of 0.5 mm were added to a vessel with the above-obtained slurry and dispersed with a disperser (1/4 G sand grinder mill, manufactured by Imex Co., Ltd.) for 5 hours, thereby a dispersion of the organic polyhalogen compound was obtained. The particles of the organic polyhalogen compound contained in the thus-obtained polyhalogen compound dispersion had an average particle diameter of 0.74 μm .

Preparation of 10 wt% Methanol Solution of Phthalazine Compound

[0227] 8-Isopropylphthalazine (10 g) was dissolved in 90 g of methanol and used.

Preparation of 20 wt% Dispersion of Pigment

[0228] Water (250 g) was added to 64 g of C.I. Pigment Blue 60 and 6.4 g of Demole N (manufactured by Kao Corporation), and thoroughly mixed to make a slurry. Zirconia beads (800 g) having an average diameter of 0.5 mm were added to a vessel with the above-obtained slurry and dispersed with a disperser (1/4 G sand grinder mill, manufactured by Imex Co., Ltd.) for 25 hours, thereby the dispersion of the pigment was obtained. The particles of the pigment contained in the thus-obtained pigment dispersion had an average particle diameter of 0.21 μm .

Preparation of 40 wt% SBR Latex

[0229] SBR Latex purified by ultrafiltration was obtained as follows.

[0230] SBR latex shown below was diluted with distilled water to 10 times, and purified by module F503-FC-FUY03A1 for ultrafiltration purification (Daisen Membrane System Co., Ltd.) until the ionic conductivity became 1.5 mS/cm. The concentration of the latex at this time was 40 wt%.

SBR Latex[0231]

Latex of -St (88)-Bu (29)-AA (3)-
Equilibrium moisture content at 25°C 60% RH: 0.6 wt%
Average particle size: 0.1 μm
Concentration: 45 wt%
Ionic conductivity: 4.2 mS/cm

Ionic conductivity was measured using a conductometer CM-30S (manufactured by Toa Denpa Kogyo Co., Ltd.), and starting solution of the latex (40 wt%) was measured at 25°C.
pH: 8.2

Preparation of Coating Solution for Emulsion Layer (photosensitive layer)

[0232] The above-obtained 20 wt% dispersion of pigment (1.1 g), 103 g of organic acid silver dispersion, 5 g of the 20 wt% aqueous solution of modified polyvinyl alcohol MP-203 (manufactured by Kuraray Co., Ltd.), 25 g of the above-prepared 25 wt% reducing agent dispersion, 11.5 g of the 30 wt% dispersion of organic polyhalogen compound, 3.1 g of the 20 wt% dispersion of mercapto compound, 106 g of the 40 wt% SBR latex purified by ultrafiltration, and 8 ml of the 10 wt% solution of phthalazine compound were mixed, thereby an organic acid silver-containing solution was obtained. Silver halide grain emulsion 1 (5 g) and silver halide emulsion 2 (5 g) had been thoroughly mixed, stirred for 20 minutes, 10 ml of distilled water had been added thereto, and mixed with the foregoing organic acid silver-containing solution immediately before coating with a stack mixer to thereby prepare an emulsion layer coating solution. This

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coating solution was fed to a coating die as it was in a coating silver amount of 1.4 g/m².

[0233] The above emulsion layer coating solution was revealed to have viscosity of 85 (mPa·s) at 40°C (No. 1 rotor) measured by Model B viscometer (manufactured by Tokyo Keiki Co., Ltd.).

[0234] The viscosity of the coating solution measured by RFS Fluid Spectrometer (manufactured by Rheometrics Far East Co.) at 25°C was 1,500, 220, 70, 40, 20 (mPa·s) at shear rate of 0.1, 1, 10, 100, 1,000 (1/sec), respectively.

Preparation of Interlayer Coating Solution of Emulsion Surface

[0235] To 772 g of polyvinyl alcohol PVA-205 (manufactured by Kuraray Co., Ltd.), 0.5 g of the 20 wt% dispersion of pigment, and 226 g of a 27.5 wt% solution of latex of methyl methacrylate/styrene/2-ethylhexyl acrylate/hydroxyethyl methacrylate/acrylic acid copolymer (copolymerization weight ratio: 59/9/28/5/1) was added 2 ml of a 5 wt% aqueous solution of Aerosol OT (manufactured by American Cyanamide Co.) to make an interlayer coating solution, which was coated in a coating amount of 10 ml/m².

[0236] The viscosity of the coating solution was 21 (mPa·s) at 40°C (No. 1 rotor) measured by Model B viscometer.

Preparation of First Protective Layer Coating Solution of Emulsion Surface

[0237] Inert gelatin (80 g) was dissolved in water, and 6 g of a toning agent (shown in Tables II-1 and II-2), 0.3 g of the 20 wt% dispersion of pigment, 28 ml of 1 N sulfuric acid, and 5 ml of a 5 wt% aqueous solution of Aerosol OT (manufactured by American Cyanamide Co.) were added thereto. Water was added to make the total amount 1,000 g, thereby a first protective layer coating solution of emulsion surface was obtained, which was coated in a coating amount of 30 ml/m².

[0238] The viscosity of the coating solution was 17 (mPa·s) at 40°C (No. 1 rotor) measured by Model B viscometer. A coating solution in which polyvinyl alcohol was used in place of gelatin was prepared.

Preparation of Second Protective Layer Coating Solution of Emulsion Surface

[0239] Inert gelatin (100 g) was dissolved in water, and 0.2 g of the 20 wt% dispersion of pigment, 20 ml of a 5 wt% solution of potassium N-perfluorooctylsulfonyle-N-propylalanine, 18 ml of a 5 wt% solution of Aerosol OT (manufactured by American Cyanamide Co.), 25 g of polymethyl methacrylate fine particles (average particle size: 4.0 μm), 44 ml of 1 N sulfuric acid, and 445 ml of a 4 wt% chrome alum were added thereto. Water was added to make the total amount 2,000 g, thereby a second protective layer coating solution was obtained, which was coated in coating amount of 20 ml/m².

[0240] The viscosity of the coating solution was 9 (mPa·s) at 40°C (No. 1 rotor) measured by Model B viscometer. A coating solution in which polyvinyl alcohol was used in place of gelatin and boric acid was used in place of chrome alum was prepared.

Preparation of PET Support

[0241] PET having an intrinsic viscosity IV = 0.66 (measured in phenol/tetrachloroethane (6/4 by weight) at 25°C) was obtained according to ordinary method using terephthalic acid and ethylene glycol. After the obtained PET was pelletized and dried at 130°C for 4 hours, melted at 300°C, extruded from T-die, and suddenly cooled, thereby an unstretched film having a film thickness after thermal fixation of 175 μm was obtained.

[0242] The film was stretched to 3.3 times in the machine direction with rollers having different peripheral speeds, then 4.5 times in the transverse direction by means of a tenter. The temperatures at that time were 110°C and 130°C respectively. Subsequently, the film was subjected to thermal fixation at 240°C for 20 seconds, then relaxation by 4% in the transverse direction at the same temperature. The chuck part of the tenter was then slit, and both edges of the film were knurled. The film was rolled at 4 kg/cm², thereby a roll of film having a thickness of 175 μm was obtained.

Corona Discharge Treatment of Support Surface

[0243] Both surfaces of the support were put under room temperature and corona discharge treatment was performed at 20 m/min with a solid state corona treating apparatus model BKVA manufactured by Piller Co. From the reading of electric current/voltage, treatment applied to the support at that time was revealed to be 0.375 kV·A·min/m². The frequency at treatment at that time was 9.6 kHz and the gap clearance between the electrode and the dielectric roll was 1.8 mm.

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Preparation of Undercoated Support(1) Undercoating5 (1-1) Undercoating Tayer Coating

[0244]

Prescription (1) (first layer)	
Butadiene/styrene copolymer latex (solid content: 43 wt%, weight ratio of butadiene/styrene: 32/68)	13 ml
8 wt% aqueous solution of sodium 2,4-dichloro-6-hydroxy-s-triazine	7 ml
1 wt% aqueous solution of sodium lauryl-benzenesulfonate	1.6 ml
Distilled water	80 ml

Prescription (2) (second layer on the photosensitive layer side)	
Gelatin	0.9 g
20 wt% dispersion of pigment	1 g
Methyl cellulose (Metolose SM15, substitution degree: 1.79 to 1.83)	0.1 g
Acetic acid (concentration: 99 wt%)	0.02 ml
Distilled water	98 ml

Prescription (3) (second layer on the back surface side)	
SnO ₂ /Sb (9/1 by weight, average particle size: 0.25 μ m)	100 mg/m ²
Gelatin	77 mg/m ²
Sodium dodecylbenzenesulfonate	1 mg/m ²
Sodium dihexyl- α -sulfosuccinate	4 mg/m ²

35 Preparation of Undercoated Support

[0245] Both surfaces of the above-prepared biaxially stretched polyethylene terephthalate support having a film thickness of 175 μ m were subjected to corona discharge treatment, then the above undercoating solution prescription (1) was coated by means of a wire bar in a wet coating amount of 6 ml/m² (per one surface side) and dried at 180°C for 5 minutes. Subsequently, one surface (photosensitive layer side) was subjected to corona discharge treatment, then the above undercoating solution prescription (2) was coated by means of a wire bar in a wet coating amount of 9 ml/m² and dried at 180°C for 5 minutes. The back surface was coated with undercoating solution prescription (3) by means of a wire bar in a wet coating amount of 5 ml/m² and dried at 180°C for 6 minutes. Thus, the undercoated support was prepared.

45 Preparation of Back Coating SolutionPreparation of Solid Fine Particle Dispersion Solution (a) of Base Precursor

[0246] A base precursor compound 11 shown below (64 g), 28 g of a diphenylsulfone compound 12 shown below, and 10 g of surfactant Demol N (manufactured by Kao Corporation) were mixed with 220 ml of distilled water. The mixed solution was dispersed using beads in a sand mill (1/4 Gallon sand grinder mill, manufactured by Imex Co., Ltd.), thereby a solid fine particle co-dispersion solution (a) of the base precursor compound and the diphenylsulfone compound having an average particle size of 0.2 μ m was obtained.

55 Preparation of Solid Fine Particle Dispersion Solution of Dye

[0247] Cyanine dye compound 13 shown below (9.8 g) and 5.8 g of sodium p-alkylbenzenesulfonate were mixed

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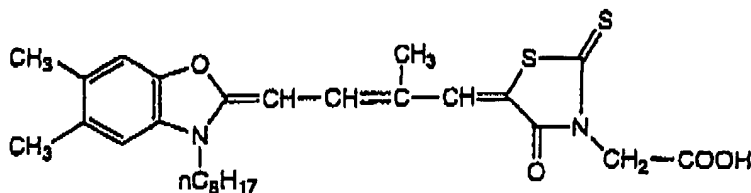
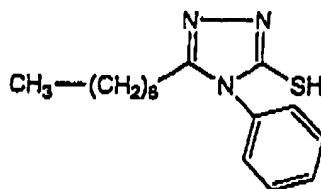
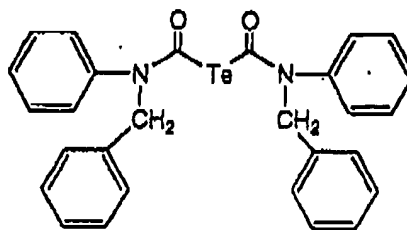
with 305 ml of distilled water. The mixed solution was dispersed using beads in a sand mill (1/4 Gallon sand grinder mill, manufactured by Imex Co., Ltd.), thereby a solid fine particle dispersion solution of the dye having an average particle size of 0.2 μm was obtained.

5 Preparation of Antihalation Layer Coating Solution

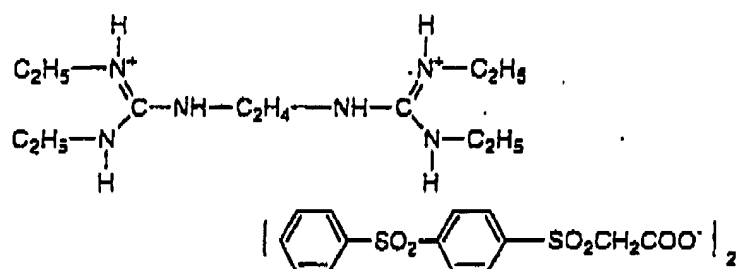
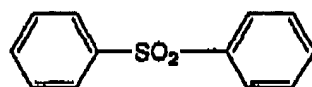
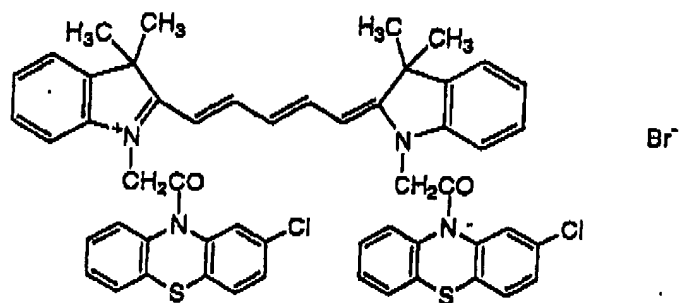
[0248] PVA-217 (17 g), 9.6 g of polyacrylamide, 70 g of the above solid fine particle dispersion solution (a) of the base precursor, 56 g of the above solid fine particle dispersion solution of the dye, 1.5 g of polymethyl methacrylate fine particles (average particle size: 6.5 μm), 2.2 g of sodium polyethylenesulfonate, 0.2 g of a coloring dye compound
10 14, and 844 ml of H_2O were mixed. Thus, an antihalation layer coating solution was prepared.

Preparation of Back Surface Protective Layer Coating Solution

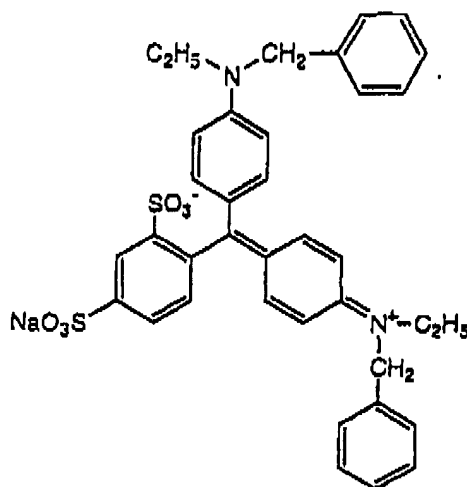
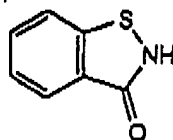
[0249] To a reaction vessel maintained at 40°C were added and mixed 50 g of PVA-117, 0.2 g of sodium polystyrenesulfonate, 2.4 g of N,N'-ethylenebis(vinyl sulfone acetamide), 1 g of sodium 1-octylphenoxyethoxyethanesulfonate, 30 mg of compound 15, 32 mg of $\text{C}_8\text{F}_{17}\text{SO}_3\text{K}$, 84 mg of $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_3\text{H}_7)(\text{CH}_2\text{CH}_2\text{O})_4(\text{CH}_2)_4\text{SO}_3\text{Na}$, 8.8 g of acrylic acid/ethyl acrylate copolymer (copolymerization weight ratio: 5/95), and 950 ml of H_2O to prepare a back surface
15 protective layer coating solution.

20 Spectral Sensitizing Dye 135 Mercapto Compound 145 Tellurium Compound

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Base Precursor Compound 11Compound 12Cyanine Dye Compound 13

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Blue Dye Compound 14Compound 15Preparation of Photothermographic (Photosensitive) Material

[0250] On the back side surface of the above-undercoated polyethylene terephthalate support, antihalation layer coating solution and the back surface protective layer coating solution were simultaneously coated and dried in such a manner that the coating amount of the solid content of the solid fine particle dye of antihalation layer coating solution became 0.04 g/m² and the PVA coating amount of the back surface protective layer coating solution became 1 g/m², thereby an antihalation backing layer was prepared.

[0251] The emulsion layer, the interlayer, the first protective layer and the second protective layer were simultaneously multilayer-coated by slide bead coating on the opposite side of the backing layer side in this order from the undercoating side, thereby photothermographic (photosensitive) material Sample was prepared.

[0252] Coating speed was 160 m/min. The distance between the tip of the coating die and the support was 0.18 mm. The pressure in the low pressure chamber was set lower than atmospheric pressure by 392 Pa. In the subsequent chilling zone, air of dry-bulb temperature of 18°C and wet-bulb temperature of 12°C was blown for 30 seconds. After the coating solution was dried, dry air of dry-bulb temperature of 30°C and wet-bulb temperature of 18°C was blown at helical floating type drying zone for 200 seconds. The sample was then passed through drying zone at 70°C for 30 seconds, and then cooled to 25°C, thereby the solvent in the coating solution was evaporated. In the chilling zone and drying zone, the average wind speed was 7 m/sec.

Evaluation of Silver Tone Due to Variation of Heat Development Condition

[0253] The sample of photothermographic photosensitive material prepared was subjected to stepwise gradation exposure with laser beams vertically multiplied by applying high frequency convolution using a semiconductor laser emitting at 660 nm. Then, heat development was performed for 20 seconds at temperatures of 117°C, 120°C and 123°C with heat developing device 10 of a plate heater type described in Fig. 1 in JP-A-11-133572, and the difference

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of silver tone due to variation of heat development condition was evaluated visually according to the following criteria. The sample was deodorized with metal mesh and an active carbon filter.

- 5 L: Difference of silver tone due to temperature condition is large and impracticable.
M: Difference of silver tone due to temperature condition is observed but in allowable range.
S: Difference of silver tone due to temperature condition is not observed and good.

Evaluation of Storage Stability

- 10 [0254] Difference in Dmin between the sample of the prepared photothermographic photosensitive material which was allowed to stand at 35°C 70% RH for 7 days and a sample which was refrigerated for 7 days was measured. Each sample was subjected to stepwise gradation exposure with a semiconductor laser emitting at 660 nm not applying high frequency convolution. Then, heat development was performed for 20 seconds at 120°C with the same heat developing device 10. Difference in Dmin was expressed as the difference in measured V value of Macbeth densitometer.
- 15 [0255] The results obtained are shown in Tables II-1 and II-2. In Table II-1, samples in which gelatin is used as the main binder in the first and second layers are shown, and in Table II-2, samples in which PVA is used as the main binder in the first and second layers are shown.

TABLE II-1

Series using gelatin in the first and second protective layers				
Sample No.	Shape of Silver Behenate	Toning Agent	Storage Stability	Silver Tone Difference
101 (Comparison)	Acicular	Phthalic acid	0.44	L
102 (Comparison)	Acicular	Ammonium phthalate	0.41	L
103 (Comparison)	Acicular	Sodium phthalate	0.40	L
104 (Comparison)	Acicular	Potassium phthalate	0.42	L
106 (Comparison)	Acicular	I-3	0.40	L
108 (Comparison)	Acicular	I-4	0.41	L
107 (Comparison)	Acicular	I-11	0.44	L
108 (Comparison)	Scaly	Phthalic acid	0.12	L
109 (Invention)	Scaly	Ammonium phthalate	0.07	S
110 (Invention)	Scaly	Sodium phthalate	0.08	M
111 (Invention)	Scaly	Potassium phthalate	0.08	M
112 (Invention)	Scaly	Lithium phthalate	0.07	M
113 (Invention)	Scaly	I-3	0.07	S
114 (Invention)	Scaly	I-4	0.08	M
115 (Invention)	Scaly	I-11	0.08	M
116 (Invention)	Scaly	I-8	0.07	M
117 (Invention)	Scaly	I-22	0.07	S
118 (Invention)	Scaly	I-13	0.07	S
119 (Invention)	Scaly	II-3	0.07	M
120 (Invention)	Scaly	II-30	0.08	M

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TABLE II-2

Series using PVA in the first and second protective layers				
Sample No.	Shape of Silver Behenate	Toning Agent	Storage Stability	Silver Tone Difference
201 (Comparison)	Acicular	Phthalic acid	0.39	L
202 (Comparison)	Acicular	Ammonium phthalate	0.36	L
203 (Comparison)	Acicular	Sodium phthalate	0.36	L
204 (Comparison)	Acicular	Potassium phthalate	0.36	L
205 (Comparison)	Acicular	I-3	0.35	L
206 (Comparison)	Acicular	I-4	0.36	L
207 (Comparison)	Acicular	I-11	0.37	L
208 (Comparison)	Scaly	Phthalic acid	0.11	L
209 (Invention)	Scaly	Ammonium phthalate	0.06	S
210 (Invention)	Scaly	Sodium phthalate	0.07	M
211 (Invention)	Scaly	Potassium phthalate	0.07	M
212 (Invention)	Scaly	Lithium phthalate	0.07	M
213 (Invention)	Scaly	I-3	0.06	S
214 (Invention)	Scaly	I-4	0.07	M
215 (Invention)	Scaly	I-11	0.07	M
216 (Invention)	Scaly	I-6	0.07	M
217 (Invention)	Scaly	I-22	0.06	S
218 (Invention)	Scaly	I-13	0.06	S

[0256] From the results in Tables II-1 and II-2, the effect of the present invention is apparent. Samples according to the present invention are excellent in photographic properties.

EXAMPLE II-2

[0257] Samples were prepared in the same manner as in Examples II-1 except that the content of stearic acid was varied (shown in Table II-3) when scaly organic acid silver was prepared, and evaluated in the same manner as in Example II-1. The results obtained are shown in Table II-3. In any sample, PVA was used as the main binder in the first and second protective layers.

TABLE II-3

Series using PVA in the first and second protective layers				
Sample No.	Content of Silver Behenate (mol%) (remaining is silver stearate)	Toning Agent	Storage Stability	Silver Tone Difference
301 (Comparison)	100	Phthalic acid	0.11	L
302 (Invention)	100	Ammonium phthalate	0.06	S
303 (Invention)	100	Sodium phthalate	0.07	M
304 (Invention)	100	I-3	0.06	S
305 (Invention)	100	I-11	0.06	M

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TABLE II-3 (continued)

Series using PVA in the first and second protective layers				
Sample No.	Content of Silver Behenate (mol%) (remaining is silver stearate)	Toning Agent	Storage Stability	Silver Tone Difference
306 (Comparison)	95	Phthalic acid	0.12	L
307 (Invention)	95	Ammonium phthalate	0.07	S
308 (Invention)	95	Sodium phthalate	0.08	M
309 (Invention)	95	I-3	0.07	S
310 (Invention)	95	I-11	0.07	M
311 (Comparison)	85	Phthalic acid	0.26	S
312 (Invention)	85	Ammonium phthalate	0.20	S
313 (Invention)	85	Sodium phthalate	0.22	S
314 (Invention)	85	I-3	0.20	S
315 (Invention)	85	I-11	0.20	S
316 (Comparison)	75	Phthalic acid	0.38	S
317 (Invention)	75	Ammonium phthalate	0.32	S
318 (Invention)	75	Sodium phthalate	0.31	S
319 (Invention)	75	I-3	0.31	S
320 (Invention)	75	I-11	0.31	S

[0258] The results in Table II-3 indicate that the storage stability is improved by increasing the content of silver behenate.

EXAMPLE II-3

[0259] Samples were prepared in the same manner as in Examples II-1 and II-2 except that SBR latex used in emulsion layers was not purified.

[0260] The same results as in Examples II-1 and II-2 were obtained.

EXAMPLE II-4

[0261] Samples were prepared in the same manner as in Example II-1 except that latexes Lb1 and Lc1 (equilibrium moisture content at 25°C 60% RH was less than 2 wt% with both Lb1 and Lc1) shown below were used in place of SBR latex used in emulsion layers.

[0262] The same results as in Example II-1 were obtained.

Synthesis of Lb1

[0263] Into a glass autoclave (TEM-V1000, manufactured by Taiatsu Glass Kogyo Co., Ltd.) were put 140 g of styrene, 280 g of distilled water, 4.44 g of a surfactant (Sandet BL, manufactured by Sanyo Kasel Co., Ltd.), and 6 g of acrylic acid, and the content was stirred for 1 hour in a nitrogen atmosphere. Thereafter, 54 g of 2-ethylhexyl acrylate was added to the reaction mixture and the temperature was raised to 70°C. Then, 20 g of a 5 wt% aqueous ammonium persulfate solution was added thereto and stirring was continued for 10 hours. After stirring was finished, the temperature of the reaction vessel was lowered to room temperature, thereby a styrene-acryl latex was obtained. 1 N aqueous ammonia was added to this latex to adjust pH to 7.5.

[0264] Thus, latex Lb1 having an average particle diameter of 98 nm and concentration of 42 wt% was obtained. Equilibrium moisture content of the polymer at 25°C 60% RH was 0.7 wt%.

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Synthesis of Lc1

[0265] Into a glass autoclave (TEM-V1000, manufactured by Taiatsu Glass Kogyo Co., Ltd.) were put 126 g of methyl methacrylate, 280 g of distilled water, 8.2 g of a surfactant (Sandet BL, manufactured by Sanyo Kasei Co., Ltd.), and 4 g of acrylic acid, and the content was stirred for 1 hour in a nitrogen atmosphere. Thereafter, 70 g of ethyl acrylate was added to the reaction mixture and the temperature was raised to 60°C. Then, 20 g of a 5 wt% aqueous potassium persulfate solution was added thereto and stirring was continued for 10 hours. After stirring was finished, the temperature of the reaction vessel was lowered to room temperature, thereby an acryl latex was obtained. 1 N aqueous ammonia was added to this latex to adjust pH to 7.5.

[0266] Thus, latex Lc1 having an average particle diameter of 101 nm and concentration of 44 wt% was obtained. Equilibrium moisture content of the polymer at 25°C 60% RH was 0.7 wt%.

EXAMPLE II-5

[0267] Samples were prepared in the same manner as in Examples II-1 to II-4 except that photosensitive silver halide was excluded. The obtained samples were heated to 100°C or more with a thermosensitive type thermal head (maximum temperature: 230°C). The same results as in Examples II-1 to II-4 were obtained.

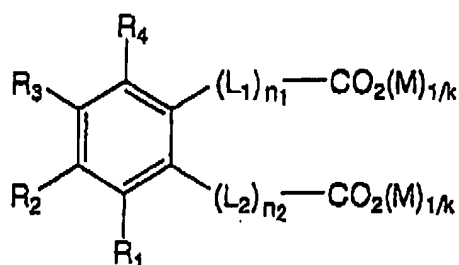
EFFECT OF THE INVENTION

[0268] According to the method of the present invention, the storage stability of a coated bulk product and silver tone can be improved.

Claims

1. An image-recording material which has at least on one surface side of a support a thermosensitive recording element containing a scaly organic acid silver salt, a reducing agent for a silver ion, and a binder, or a photosensitive recording element containing a scaly organic acid silver salt, a reducing agent for a silver ion, photosensitive silver halide, and a binder, wherein the NH_4^+ content of all the layers on the surface side of the support which has the thermosensitive or photosensitive recording element is from 0.06 to 3.4 mmol as the coating amount per m^2 of the support.
2. The material as claimed in claim 1, wherein the NH_4^+ content is from 0.55 to 2.8 mmol as the coating amount per m^2 of the support.
3. The material as claimed in claim 1 or 2, wherein the alkali metal ion content of all the layers on the surface side of the support which has the thermosensitive or photosensitive recording element is from 0.05 to 3.6 mmol as the coating amount per m^2 of the support.
4. The material as claimed in claim 3, wherein the alkali metal ion content is from 0.59 to 3.0 mmol as the coating amount per m^2 of the support.
5. The material as claimed in claim 3 or 4, wherein said alkali metal ion is Li^+ , Na^+ , or K^+ .
6. The material as claimed in any of claims 3 to 5, wherein the ratio of the contents of said alkali metal ion and NH_4^+ is in molar ratio of $(\text{NH}_4^+)/(\text{alkali metal ion})$ of from 0.01 to 30.
7. The material as claimed in any of claims 3 to 5, wherein the ratio of $(\text{NH}_4^+)/(\text{alkali metal ion})$ is from 0.1 to 20.
8. The material as claimed in any of claims 3 to 5, wherein the ratio of $(\text{NH}_4^+)/(\text{alkali metal ion})$ is from 0.6 to 5.
9. The material as claimed in any claims 1 to 8, wherein the layer containing a scaly organic acid silver salt further contains a phthalic acid compound represented by formula (I):

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(I)

wherein R_1 , R_2 , R_3 and R_4 each represents a hydrogen atom or a monovalent substituent; L_1 and L_2 each represents a linking group; n_1 and n_2 each represents 0 or 1; M represents a hydrogen atom or a counter ion; and k represents a valency of M , and when M represents a hydrogen atom, k represents 1, provided that when M represents a hydrogen atom and n_1 and n_2 each represents 0, not all R_1 , R_2 , R_3 and R_4 represent a hydrogen atom.

10. The material as claimed in claim 9, wherein M in formula (I) represents an ammonium ion, an alkali metal ion, an alkaline earth metal ion, an aluminum ion, a zinc ion, an ionic polymer, an organic compound having reverse charge, or a metal complex ion.

11. The material as claimed in any of claims 1 to 10, wherein the silver behenate acid content of the organic acid silver salt is 92 mol% or more.

12. The material as claimed in any of claims 1 to 11, wherein the layer containing the said organic acid silver salt is formed by coating a coating solution in which 30% by weight or more of the solvent is occupied by water, and then drying, and the main binder of this layer is a polymer having an equilibrium moisture content at 25°C 80% RH of 2% by weight or less.

13. The material as claimed in any of claims 1 to 12, wherein the material contains a photosensitive recording element.

14. The material as claimed in claim 13, wherein the material has two or more constitutional layers including said photosensitive recording element on the same surface side of the support on which said photosensitive recording element is provided and these two or more constitutional layers are simultaneously coated.

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FIG. 1

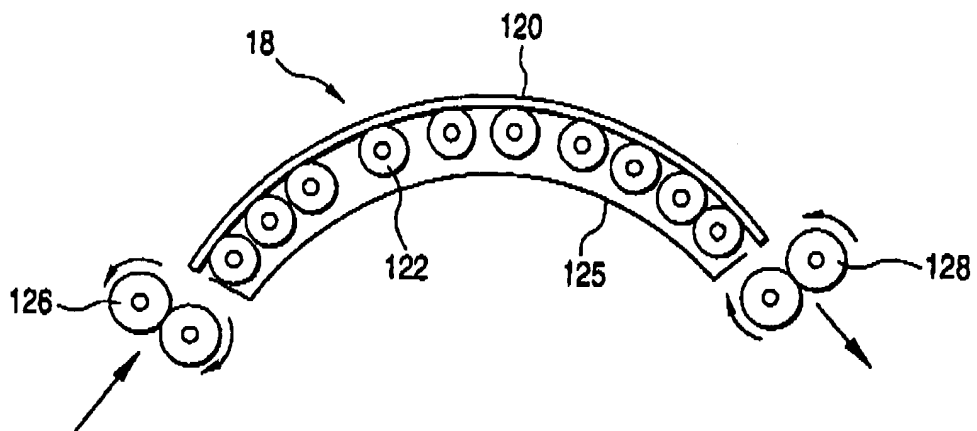
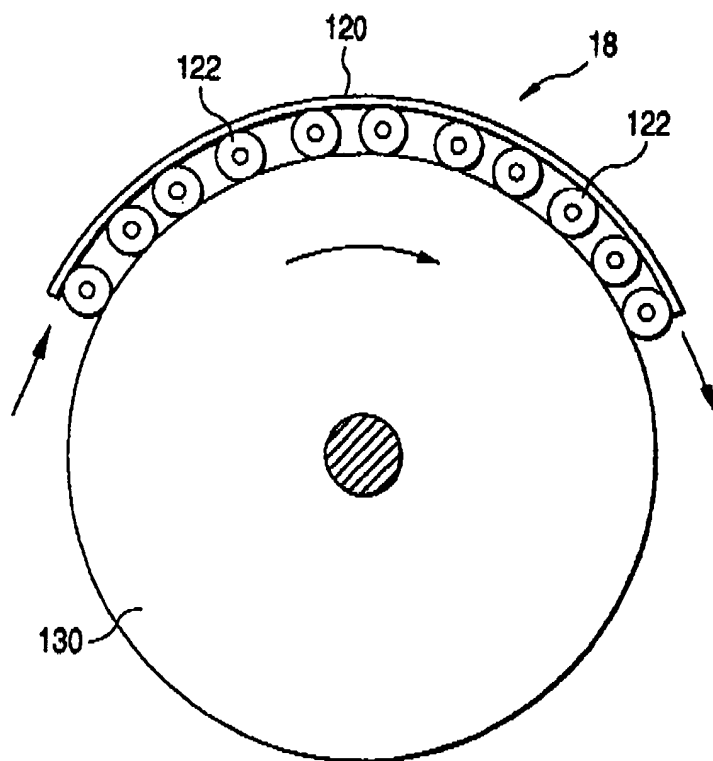


FIG. 2



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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 99 12 5508

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (InCL.7)
P, A	EP 0 962 812 A (FUJI PHOTO FILM CO LTD) 8 December 1999 (1999-12-08) * see claim 14; page 8, line 57 to page 9, line 30 and examples *	1-14	603C1/498
A	EP 0 754 969 A (AGFA GEVAERT NV) 22 January 1997 (1997-01-22) * see column 4, lines 12-24; claims 15 and 16 and examples *	1-14	
			TECHNICAL FIELDS SEARCHED (InCL.7)
			603C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 3 May 2000	Examiner Okunowski, F
CATEGORY OF CITED DOCUMENTS		Y: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons A: member of the same patent family, corresponding document	
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 12 5508

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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03-05-2000

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